Green Synthesis of Cobalt Sulphide as an Electrode Material for Supercapacitor Application

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by

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ABSTRACT

The development of supercapacitive electrode materials through simple, reasonably priced, and industrially scalable deposition processes to use in energy storage devices. The metal sulphide have been successfully employed as electrode materials that could be used in supercapacitors. The methodology described in this work offers creating affordable and environmentally friendly energy storage solutions using plant with a particular emphasis on cobalt sulphide from Tridax Procumbens plants for supercapacitor electrodes. Tridax procumbens, a widely available medicinal plant, contains bioactive compounds such as flavonoids, alkaloids, tannins, and phenolics, which can act as reducing and stabilizing agents in nanoparticle synthesis. By utilizing it as electrode material Tridax Procumbens plant is transformed into cobalt sulphide by green synthesis. XRD techniques are utilized to characterize the material. Using techniques such as electrochemical impedance spectroscopy (EIS), galvanostatic charge–discharge (GCD), and cyclic voltammetry (CV), the electrochemical performance of the Cobalt Sulphide based electrode was thoroughly examined. From CV and GCD curves, the electrodes show pseudocapacitive behaviour. In GCD analysis, the CoS_2 electrode shows the highest specific capacitance 604.47 F g^{-1} at 12 A g^{-1} in 3M KOH electrolyte. The electrochemical energy storage capability studies showed that the CoS_2 NPs annealed at 300 °C gives the best specific capacitance of 1612 F g^{-1} at 5 mV s^{-1}.

List of Figures

Figure no.	Title	Page no.
1.1	Types of Energy Storage Devices	19
1.2	Advantages of Supercapacitor	20
1.3	Renewable energies & supercapacitors applications	22
1.4	RAGONE PLOT	25
1.5	Classification of Supercapacitor	27
1.6	Model for electrical double layer:(a) The Helmholtz model (b) The Gouy Chapman model (c) The Stern model	30
1.7	Hybrids SC	32
1.8	Different Electrode Material for Supercapacitor	34
1.9	Schematic presentation of challenges and future aspects for metal sulfides as energy material	41
1.10	Number of publications for metal sulfides as supercapacitor	41
3.1	Tridax Procumbens Plant	48
3.2	Green synthesis of Cobalt Sulfide NPs using Tridax procumbens leaf extract	51
3.3	Schematic diagram of fabrication of Cobalt Sulphide based electrode	52
3.4	Schematic diagram of x-ray diffractometer	53
3.5	Instrumentation and working of Scanning Electron Microscopy	54
3.6	Schematic diagram of electrochemical setup	55
3.7	Cyclic voltammogram	56
3.8	Charging and discharging mechanism (a) EDLC and (b) Pseudocapacitor	58
3.9	Electrochemical impedance spectroscopy	59
4.1	XRD Spectra of the CoS_2 Sample	60
4.2	SEM image of CoS_2 electrode	61
4.3	EDS Spectrum of CoS_2 Nanoparticles	62
4.4	CV curves at variable scan rates	63

4.5	Specific Capa. Vs Scanning Rates	64
4.6	GCD curves at different current density	65
4.7	Specific Capa. Vs Current Density	65
4.8	Nyquist plot of CoS_2-based electrode.	67
4.9	Bode Phase Plot of CoS_2-based electrode	67
4.10	Cycling stability of CoS_2 based electrode	68

List of Tables

Table no.	Title	Page no.
1	Comparison between Different Energy Storage Devices	27
2	Atomic weight % of elements in CoS_2 NPs	61
3	Specific Capacitance of CoS_2 electrode at different scan rates	64
4	Specific Capacitance of CoS_2 electrodes at different Current Density	66

List of Abbreviation

Abbreviation	Full form
EDLC	Electric Double Layer Capacitor
SCs	Supercapacitor
CNTs	Carbon Nanotubes
CNFs	Carbon Nanofibers
AC	Activated Carbon
PVDF	Polyvinylidene Fluoride
NMP	N- Methyl-2-Pyrrolidone
DI Water	Deionized water
PVDF	Polyvinylidene Fluoride
NMP	N- Methyl-2-Pyrrolidone
HCl	Hydrochloric acid
ESR	Equivalent Series Resistance
AC	Activated Carbon
CNTs	Carbon Nanotubes
CNFs	Carbon Nanofibers
PC	Pseudocapacitor
MCs	Metal Chalcogenides
MSs	Metal Sulphide
MOs	Metal Oxide
XRD	X-ray Diffraction Analysis
CV	Cyclic Voltammetry
GCD	Galvanostatic Charge - Discharge
EIS	Electrochemical Impedance Spectroscopy

List of Symbol

Symbol	Meaning
C	Capacitance
Q	Charge
V	Potential
ε_0	Permittivity of free space
ε_r	Dielectric Constant
A	Area of plate of Capacitor
d	Distance between plate of Capacitor
U	Energy stored in Capacitor
Pmax	Maximum Power
Cs	Specific Capacitance
Im	Current density
Δt	Discharge time
ΔV	Potential window
ED	Energy density
PD	Power density

CONTENTS

Abstract I

List of Figure II

List of Tables III

List of Abbreviation IV

List of Symbols V

Contents

1. INTRODUCTION

1.1 General Introduction

1.2 History of Supercapacitor

1.3 Electrochemical storage devices

1.4 Supercapacitor

1.5 Application of Supercapacitor

1.6 Comparison Between Capacitor, Supercapacitor and Battery

1.7 Classification of Supercapacitor

1.7.1 Electric Double Layer Capacitor

1.7.2 Pseudo Capacitor

1.7.3 Hybrids SC

1.7.3.1 Composite Hybrids SC

1.7.3.2 Asymmetric Hybrids SC

1.7.3.3 Battery Type Hybrids SC

1.8 Electrode material

1.8.1 Carbon based material

1.8.1.1 Graphene

1.8.1.2 Carbon Nanotubes

1.8.1.3 Carbon Nanofibers

1.8.1.4 Activated Carbon

1.8.2 Metal Oxides

1.8.3 Metal Chalcogenides

1.8.4 Metal Sulphide

1.9 Electrolyte

1.10 Aim and Objective of this present work-

2. LITERATURE SURVEY

3. EXPERIMENTAL WORK

3.1 Tridax procumbens

3.2 Advantages of Tridax Procumbens

3.3 Method of Cobalt Sulphide synthesis

3.4 Green Synthesis of Cobalt Sulphide

3.5 Material used-

3.6 Preparation of Tridax Procumbens Plant Extract

3.7 Synthesis of Cobalt Sulphide NPs

3.8 Fabrication of Cobalt Sulphide Material Electrode

3.9 Characterization Techniques

3.9.1 Xray- Diffraction (XRD)

3.9.2 Scanning Electron Microscopy (SEM)

3.9.3 Energy -Dispersive X-ray Spectroscopy (EDS)

3.10 Potentiostat for Electrochemical performance

3.11 Electrochemical measurements

3.11.1 Cyclic voltammetry (CV)

3.11.2 Galvanostatic charge-discharge (GCD)

3.11.3 Electrochemical impedance spectroscopy (EIS)

4. RESULT AND DISCUSSION

4.1 Structural Characterization

4.1.1 X-ray Diffraction Analysis-

4.2 Morphological Characterization

4.2.1 Scanning Electron Microscopy –

4.2.2 Energy-Dispersive X-ray Spectroscopy-

4.3 Electrochemical characterization

4.3.1 Cyclic Voltammetry

4.3.2 Galvanostatic Charge-Discharge Analysis-

4.3.3 Electrochemical impedance spectroscopy

4.3.4 Cyclic Stability

5. CONCLUSION

6. REFERENCES

CHAPTER 1: INTRODUCTION

1.1 General Introduction

Energy is a fundamental necessity throughout modern life, playing a major role in both domestic and industrial relevance. Global economic growth rapidly increased energy demand greatly so we depend substantially on coal, oil, natural gas and fossil fuels. However, this reliance produces two critical issues which badly cause danger to energy security also the environment. The diminution of fossil fuel reserves is the first concern in that. As these resources are finite as well as non-renewable, their availability reduces, meaning that as they continue to be obtained and utilized at high rates. Result in increasing costs and potential energy shortages in the future.

Many studies expect that if current ingesting trends continue, fossil fuel supplies could become significantly low within the upcoming years, making it necessary to find alternative energy solutions. The second concern is relates environmental effect of fossil fuel consumption. The burning of coal, natural gas and oil releases huge amounts of greenhouse gases, mainly carbon dioxide (CO_2), into the atmosphere. This pays to global warming and climate change, subsequent in extreme weather conditions, rising sea levels, and disturbances to ecosystems. Furthermore, using fossil fuels and the release of greenhouse gases pollutes the air, contaminates water and causes other environmental problems that shows effect on human health and biodiversity.

All these challenges have increased the demand for renewable and environmentally friendly energy sources. Renewable energy sources for example hydro, wind, biomass, and solar offer a viable and more sustainable alternative to fossil fuels. Renewable energy sources neither diminish over time unlike conventional energy sources nor emit harmful pollutants. These renewable energy systems are more affordable, effective and available across the world. Adopting renewable energy helps solve the energy crisis, supports economic stability and protects the environment. With continued research, innovation and investment, renewable energy provides the world's growing energy needs and ensures a healthier planet for future generations

Energy consumption and production, which are mostly dependent on burning fossil fuels, have a big effect on the environment and the world economy. As a result, there is a increasing need for energy storage devices that are cost-effective, high-performance and environmentally friendly energy storage devices to support the transition to renewable energy sources. Supercapacitors (SCs) stand out among energy storage devices because their outstanding energy storage properties and high-power density. SCs have several advantages over traditional energy storage devices, including high power output, long life cycles, enhanced specific capacitance, outstanding performance and environmental friendliness. Not only that, but they can also work effectively in a broad spectrum of temperatures. The remarkable characteristics of SCs is their rapid charging capability and almost instantaneous energy delivery, which allows them to serve as a final intermediary between conventional capacitors and batteries. Because of these features, supercapacitors are ideal for remote and rural areas with limited network access or where building power infrastructure is too expensive. With its fast charge–discharge capability and high durability further enhance their appeal as a sustainable energy storage solution for modern[1].

1.2 History of Supercapacitor

In 1966, a team of researchers developed an early prototype at Standard Oil of Ohio (SOHIO) of what would later be recognized as an electrochemical capacitor. This device was introduced under the Despite its potential, the patent filed at the time did not elaborate on the electrochemical principles underlying the energy storage mechanism, leaving the scientific basis mainly unexplored. Later, in 1970, Donald L. Boos was granted a patent for a similar device that incorporated activated carbon electrodes. Although this design closely resembled what we now identify as an electrochemical capacitor, it was still officially classified as an electrolytic capacitor[2], [3].

Early electrochemical capacitors, which later evolved into what we now call supercapacitors, were constructed using a relatively simple yet effective design. These devices typically consisted of two aluminium foils serving as current collectors, each coated with a layer of activated carbon, which behaved as the electrodes. The activated carbon, due to this it’s extremely elevated surface area and porous structure, performed a fundamental role in enhancing the charge storage capacity. Between the two electrodes, a

thin, porous separator was placed to prevent electrical short circuits while allowing ion movement. This entire assembly was soaked in an electrolyte solution that cause ionic conduction between the electrodes[4]. This design permitted for the creation of electric double layers at the interface between the electrolyte and activated carbon, thereby substantially increasing the capacitance. The resulting capacitance could affect values in the range of one farad or more, which was orders of magnitude greater than conventional electrolytic capacitors of comparable size. The high energy density, coupled with quick charge/discharge experiences, made this design highly beneficial for various applications[4].

Although this modern capacitor structure was developed by SOHIO (Standard Oil of Ohio), the company did not pursue its commercial potential directly. Instead, SOHIO licensed the technology to NEC, a Japanese electronics corporation. NEC refined and commercialized the technology, and in 1978, they initiated it to the market under the name "supercapacitors." These early supercapacitors were essentially used to supply backup power for volatile memory in computers, ensuring data retention during short power interruptions. Brian Evans Conway carried out extensive and pioneering research proceeding electrochemical capacitors between 1975 and 1980, focusing particularly on ruthenium oxide-based systems. His work laid the foundation for the expansion of high-performance energy storage devices. In 1991, Conway complete a significant involvement to the understanding of electrochemical energy storage by clearly distinguishing between "supercapacitor" and "battery" behaviour. He emphasized that while batteries store energy mostly through bulk faradaic (redox) reactions, supercapacitors merge non-faradaic and faradaic processes for energy storage.

In 1999, Conway formally introduced and defined the term "supercapacitor" to describe energy storage devices that exhibit an enhanced capacitance due to surface redox reactions. These reactions concern faradaic charge transfer involving the electrode material and electrolyte ions, a process now known as pseudocapacitance. In a supercapacitor, electrical charge is stored partially through electrostatic accumulation at the electrode and electrolyte interface forming the Helmholtz double layer and partially through faradaic processes involving reversible redox reactions at the surface or near-surface of the electrode. Brian Evans Conway significantly advanced the scientific

understanding of electrochemical capacitors and placed the conceptual groundwork for the growth of modern supercapacitor technologies[5].

By the late 1980s, significant advancements in electrode materials led to notable upgrading in the capacitance of electrochemical capacitors. These new materials proposed higher surface areas and improved electrochemical activity, thereby increasing the amount of electrical charge that could be stored. Simultaneously, the advancement of advanced electrolytes by higher ionic conductivity participated to a reduction in the equivalent series resistance (ESR) of the devices. This improvement supported higher charge and discharge currents, making the capacitors more efficient for various applications. A major milestone in supercapacitor technology was achieved in 1982 when the Pinnacle Research Institute (PRI) first developed supercapacitor analysed by a minimal internal resistance, specifically tailored for military purposes. These products were marketed under the "PRI Ultracapacitor" brand and were an early example of high-performance supercapacitors that could handle demanding power delivery and energy storage applications. Maxwell made the term "Ultracapacitor," which was first used by PRI, widely known. Maxwell changed their product line to "Boost Caps," emphasizing the devices' capacity to provide quick energy bursts, to highlight their feasibility for high-power applications[6].

The main benefits of electrolytic and electrochemical capacitors were combined in the design of the electrolytic-hybrid electrochemical capacitor. In particular, it combined the high pseudocapacitance offered by a metal oxide cathode—specifically, ruthenium (IV) oxide (RuO_2), a well-known substance utilized in electrochemical capacitors—with the high dielectric strength of a conventional electrolytic capacitor anode[7].

The theory of the electric double layer was introduced first in 1853 by the German physicist Hermann von Helmholtz. Over time, this concept evolved into the enhancement of electric double layer capacitors (EDLCs), which are commonly used today for efficient energy storage applications due to their high power density and rapid charge-discharge abilities. The development of electrolytic capacitors began in the 1920s, a breakthrough occurred in 1957 when General Electric became the first company to manufacture large-scale EDLCs. They utilized activated carbon as the electrode material, capitalizing on its high surface area to significantly enhance charge storage capacity. This

innovation paved the way for the modern use of supercapacitors in various fields, from portable electronics to energy recovery systems[8], [9].

1.3 Electrochemical storage devices

Since electrochemical energy storage technologies offer dependable and effective ways to store electrical energy, they are crucial parts of today's energy landscape. Numerous applications, from commonplace portable electronics to cutting-edge electric cars and massive energy storage for power grid stabilization, make extensive use of these technologies. The most widely used electrochemical storage systems are batteries and capacitors, out of all the other kinds.

Battery - To properly absorb and release energy, batteries store energy through reversible electrochemical reactions. One or more electrochemical cells make up a standard battery. Each cell has three basic parts: an anode (negative electrode), a cathode (positive electrode), and an electrolyte that helps ions travel between the two electrodes. In order to maintain charge balance during the charging process, ions in the electrolyte move in tandem with electrons that are driven from the cathode to the anode via an external circuit by an external power source. This process allows the cell to store energy as chemical potential. When the battery is discharged, the stored chemical energy is converted back into electrical energy as electrons flow from the anode to the cathode through the external circuit, generating a usable electric current. This reversible flow of electrons and ions is what permits the battery to be recharged and reused multiple times[10].

Fuel cells - Fuel cells are energy-conversion devices that use an electrochemical reaction to directly convert a fuel's chemical energy into electrical energy. A constant supply of fuel (usually hydrogen) and an oxidizing agent (such oxygen from the air) is maintained, fuel cells may continually generate electricity, in contrast to batteries, which have a limited internal chemical energy storage capacity and must be recharged once it is used up. Due to their capacity to run continuously, fuel cells can supply a consistent and dependable power source, which makes them appropriate for a range of uses, from large-scale power systems to portable gadgets. The electrochemical process in fuel cells involves the oxidation of fuel at the anode and the reduction of the oxidizer at the

cathode, with the movement of electrons through an external circuit generating usable electric current.

Capacitors - An electric field developed between two conducting plates spaced apart by a dielectric (insulating) substance allows electrical energy to be electrostatically stored in capacitors, which are energy storage devices. Capacitors store and release energy quickly, which makes them perfect for applications that demand short bursts of power. Batteries store energy chemically. They play a major role in many electrical and electronic systems, including as filtering in electronic circuits, power conditioning, voltage management, and signal processing. Capacitors are also important components of energy harvesting systems and temporary energy storage systems. Their ability to deliver high power density and respond almost instantaneously to changes in voltage makes them particularly valuable in specialized applications such as camera flashes, regenerative braking systems in electric vehicles, pulsed power systems, and backup power supplies. This fast charge and discharge capability allows capacitors to enhance the efficiency and performance of countless modern technological systems.

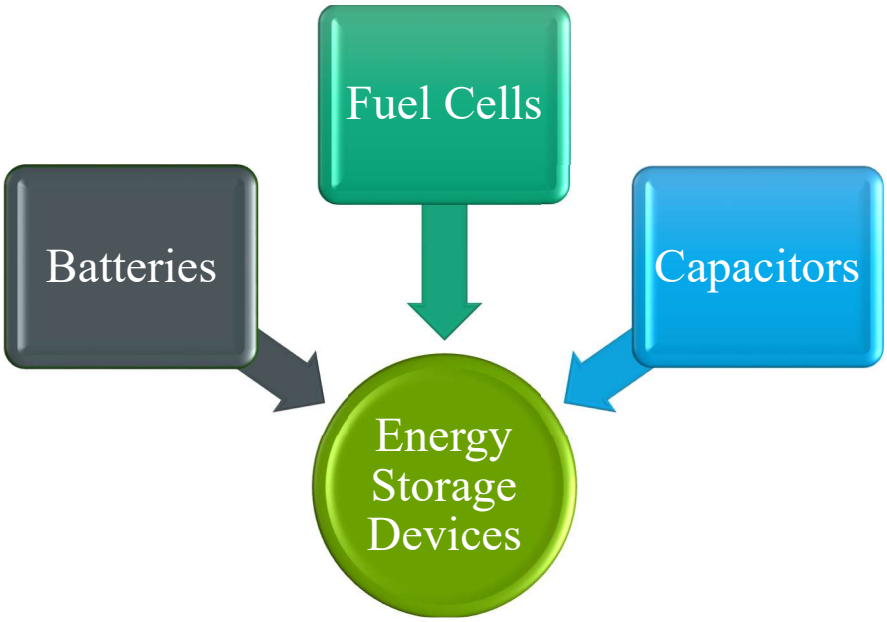

Fig. 1.1 Types of Energy Storage Devices

1.4 SUPERCAPACITOR

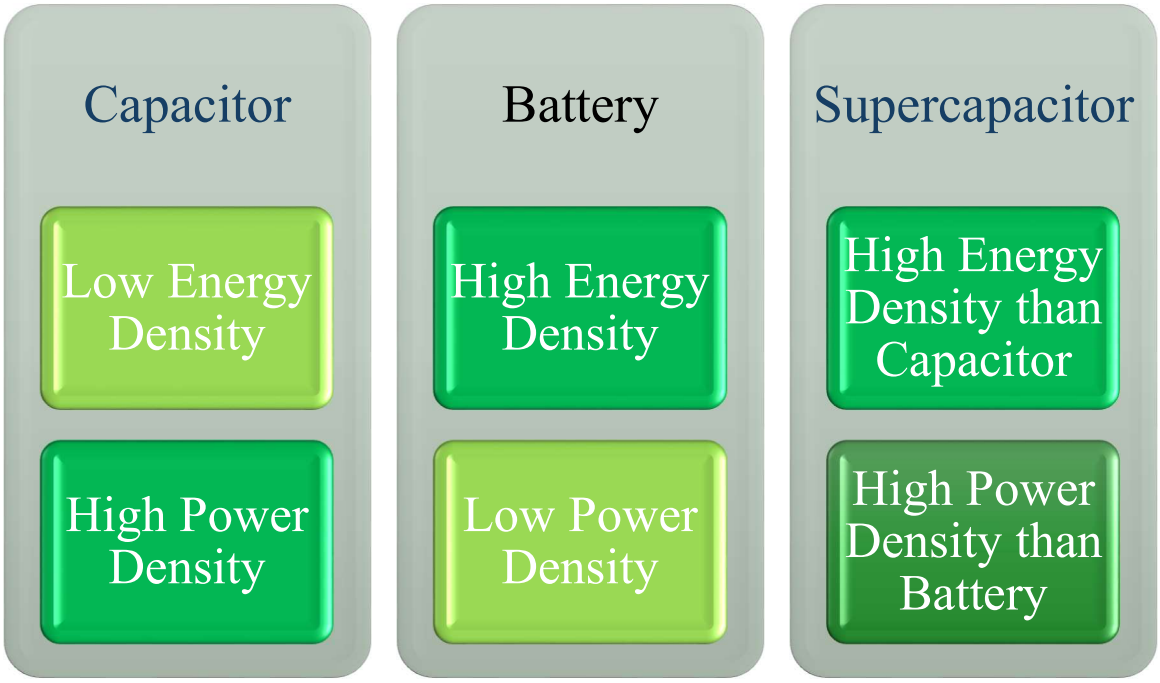

Fig. 1.2 Advantages of Supercapacitor

Supercapacitors, also known as ultracapacitors that have a capacitance that is significantly higher than that of conventional solid-state capacitors. Although they operate at lower voltages, supercapacitors can store significantly more energy than standard capacitors. They bridge the gap between electrolytic capacitors and rechargeable batteries by combining the strengths of both. Compared to conventional electrolytic capacitors, they may store 10–100 times as much energy per unit mass or volume. Supercapacitors can deliver and absorb energy much faster than batteries because of their quick charge and discharge ability. They also last much longer, handling many more charge-discharge cycles without losing performance, making them ideal for uses that need frequent and fast energy delivery[11].

Electrostatic double-layer capacitance and electrochemical pseudocapacitance are the two charge storage methods used by supercapacitors. Capacitors use a solid dielectric

material to store electrical energy. Instead of using a traditional dielectric, supercapacitors use the interface between an electrode and an electrolyte to form an electric double layer. SCs also use pseudocapacitance, which results from quick and reversible redox (reduction-oxidation) reactions at the electrode surface, in addition to this physical mechanism. Together, the two processes greatly increase the supercapacitor's overall energy storage capacity[12].

Supercapacitors have electrodes with a much larger surface area, and their insulating layers are very thin. This reduces the distance between the electrodes, which helps them store more charge more efficiently.

1.5 Application of Supercapacitor

Supercapacitors have received considerable attention in recent years. This is due to their unique electrochemical characteristics, especially in the context of renewable energy management and storage. Supercapacitors are ideal for different applications such as electric vehicles, wearable electronics and portable electronics as it provide effective energy uptake and delivery. Furthermore, the wide range of supercapacitor configurations and sizes allows for a greater degree of flexibility in many technological and industrial applications.

Supercapacitors have a long cycle life, allowing them to withstand almost an infinite number of fast charge–discharge cycles with little to no degradation. Supercapacitors (SCs) are increasingly being utilized in hybrid electric vehicles (HEVs), electric grid, rail systems and electric vehicles (EVs) due to their ability to improve energy efficiency and dependability. They are also use in portable electronic devices such computer, digital cameras, smartphones and some other electronics devices due to their small size and adaptable construction. SCs are reliable sources of power in these applications, able to provide consistent action over time, as well as bursts of fast energy.

Additionally, their relatively small manufacturing cost and modular design facilitate ease of integration and scalability within complex energy systems. Other advantageous features include minimal maintenance requirements, robust operational stability, and environmental sustainability. These attributes collectively underscore the

growing relevance of supercapacitors as a vital component in the advancement of next-generation energy storage technologies[13].

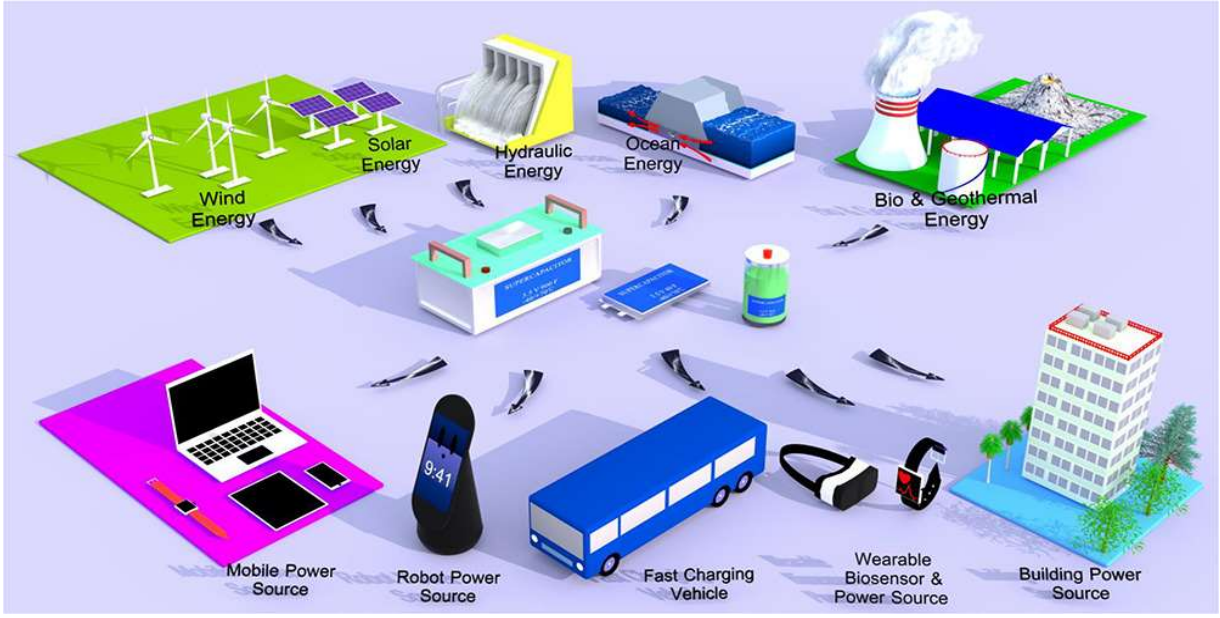

Fig. 1.3 Renewable energies & supercapacitors applications [13]

1.6 Comparison Between Capacitor, Supercapacitor and Battery

Electrostatic capacitors with a dry separator, electrolytic capacitors with a wet separator, and supercapacitors are the three main types of capacitors that are often distinguished by their construction and functionality.

Electrostatic Capacitors: A dry dielectric substance is used between the plates of electrostatic capacitors, which are conventional capacitors. Usually, they deliver capacitance values between a few picofarads (pF) and a few microfarads (µF), which is a rather low value. They are common in electrical circuits for applications like radio frequency tuning and signal filtering, where accurate and tiny capacitance values are crucial, even though they have a limited store capacity.

Electrolytic Capacitors: Unlike electrostatic capacitors, these capacitors have a moist separator drenched in an electrolyte, which greatly increases their capacitance. For the most part, their capacitance falls between a few microfarads and thousands of microfarads. Signal coupling and decoupling, voltage buffering, and power supply filtering are the main uses for electrolytic capacitors. For energy-intensive applications,

they are perfect since they have a storage capacity that is around 1000 times greater than that of electrostatic capacitors of the same size.

Supercapacitors combine electrostatic and electrochemical processes to store energy, whereas parallel plate capacitors are one based on the electrostatic separation of charges over a dielectric medium. At the electrode–electrolyte interface, this involves the creation of electric double layers and, occasionally, pseudocapacitive processes. Supercapacitors can achieve capacitance values that are orders of magnitude higher than those of conventional capacitors, also enable to achieve a substantially larger surface area and a shorter effective charge separation distance[14].

A dielectric substance is placed in between two conducting plates to form a parallel plate capacitor. Equal and opposing charges build up on the electrode surfaces when a voltage is applied across the plates. An electric field can occur inside the dielectric material, which acts as an insulating barrier between the plates and stops immediate charge flow. For the capacitor to store electrical energy, this electric field is essential. The capacitance is the ratio of the amount of charge held on either plate to the voltage applied across the plates and its evaluate the capacity of capacitor to store charges. Mathematically, we can express this relation as-

$$C = \frac{Q}{V} \qquad \ldots (i)$$

where C is the capacitance in farads (F), Q is the stored charge in coulombs (C), and V is the potential difference in volts (V) across the capacitor[15].

Moreover, a parallel plate capacitor's capacitance (C) is inversely proportional to the distance (r) between the electrodes and directly proportional to their surface area (A). Capacitance increases with area and decreases as distance between the plates raises. The equation can be written as -

$$C = \frac{\varepsilon_0 \, \varepsilon_r \, A}{r} \qquad \ldots (\text{ii})$$

Where, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the insulating material between the plates, A is the area of one of the plates and r is the distance between the plates. This equation can give geometry of the capacitor and the properties of the dielectric material in determining the capacitance[16].

By evaluating the performance of capacitor, we can determine the energy density and power density of the capacitor. These values are used to evaluate the ability of a capacitor to store energy and to supply energy. The following equation shows the overall energy that a capacitor can store it is dependent on the capacitor's capacitance and applied voltage as-

$$E = \frac{1}{2}CV^2 \qquad \ldots (iii)$$

The electrodes, dielectric material, and current collectors are some of the internal parts of a capacitor that affect its resistance[17]. Together, these distinct resistances make up the Equivalent Series Resistance (ESR). ESR, or the capacitor's total internal resistance, is a key factor in how well it performs, especially throughout cycles of charging and discharging. This resistance also affects the maximum power output (P_{max}) that a capacitor can provide, which may be handled by taking the ESR and other operating parameters into account[18]. The maximum power Pmax of a capacitor is determined by

$$P_{max} = \frac{V^2}{4 \times ESR} \qquad \ldots (iv)$$

In contrast to electrochemical batteries and fuel cells, conventional capacitors often have lower energy densities but higher power densities. Accordingly, capacitors have a limited capacity for storing energy overall, even though they may transfer energy rapidly. However, batteries have a lower power density than capacitors since they cannot release the energy they store as quickly. Batteries can store a considerable amount extra energy than capacitors. Although capacitors have a notably smaller energy storage capacity per unit mass or volume, they excel in applications that need a rapid burst of energy since they can discharge their stored electrical energy very instantly. The components of a supercapacitor (SC) are an electrolyte, two electrodes, and a separator that electrically

isolates the two electrodes. The basic ideas behind the storage of electrical energy through charge separation are similar for both conventional capacitors and supercapacitors. Nevertheless, some upgrading made to the design of supercapacitors greatly boost their efficiency. They use amazingly thin dielectric layers, which lessen the distance between the electrodes and facilitate effective charge accumulation. They also employ electrodes with a relatively high surface area, which boosts the amount of charge that can be stored and gives them a significantly higher energy density than conventional capacitors[19].

Compared to fuel cells and electrochemical batteries, supercapacitors also have a number of advantages. These involve the potential to creäte high power densities, considerably longer cycle and shelf lives, and ultra-fast charging capabilities[20].

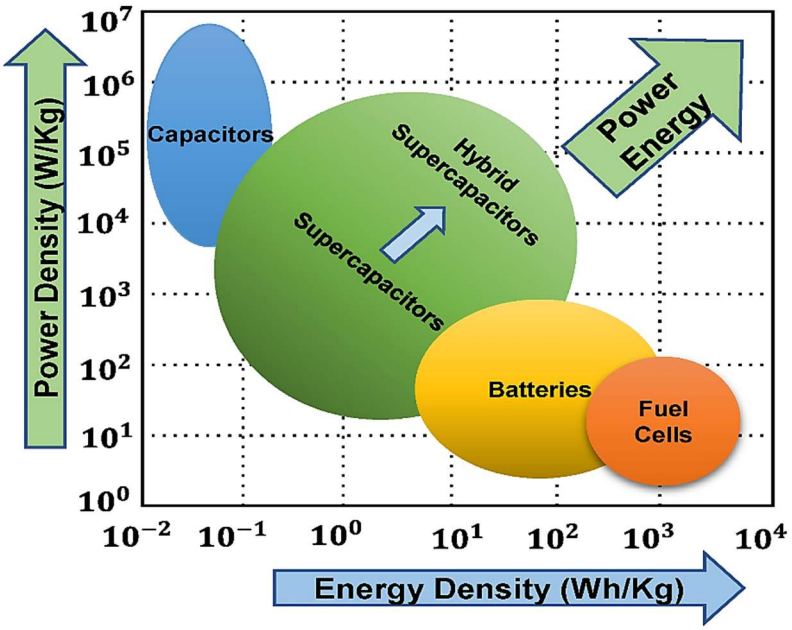

Fig. 1.4 RAGONE PLOT[21]

Table (1) - Comparison between Different Energy Storage Devices

Characteristics	Capacitor	Supercapacitor	Battery
Specific energy (Wh/kg)	<0.1	Up to 100	Up to 1.606k
Specific power (W/kg)	>10,000	Up to 196k	<1k
Charge time	10^{-6} to 10^{-3}s	s to min	1-5h
Discharge time	10^{-6} to 10^{-3}s	s to min	1 – 3h
Life Cycle	∞	>500k	About 1k
Columbic efficiency	≈ 100%	85 – 98%	70 – 85%
Operating temperature	-20 to 100°C	-40 to 85°C	-20 to 65°C

1.7 Classification of Supercapacitor

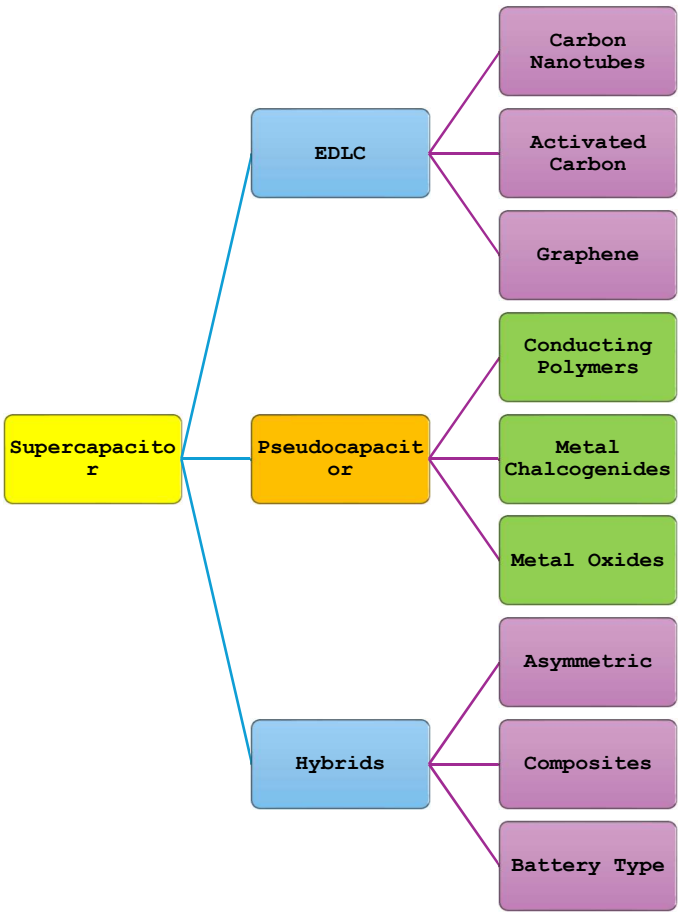

Fig. 1.5 Classification of Supercapacitor

Supercapacitors can be broadly categorized into three varieties according to how they store charge.

1.7.1 Electric Double Layer Capacitor (EDLC)

An electrolyte, two carbon-based electrodes, and a separator make up an electric double layer capacitor (EDLC). EDLCs do not entail charge transfer between the electrodes and the electrolyte, in contrast to batteries. Instead, they use a mechanism known as non-Faradaic charge storage, which include electrostatic energy storage. An electrical double layer occurs at the contact between the electrode surface and the electrolyte when a voltage is applied across the electrodes. As charges build up on the

electrode surfaces, ions from the electrolyte move through the separator and into the electrode pores, where they align with the opposing charge through electrostatic attraction.

Comparing EDLCs to conventional capacitors, this method allows a noticeably better energy density. The development of double layers, a increase in the porous electrodes effective surface area, and a reduction in the effective distance between the charges stored on the electrodes are the most important causes of the improvement. Because of its high degree of reversibility, EDLCs can be utilized for quick cycles of charging and discharging. Two electrode layers that are structurally identical and serve as the capacitor's "virtual" plates build EDLCs. However, the operating voltage that a single EDLC cell can endure is relatively low. The individual voltages of several EDLC cells are coupled in series to generate the larger voltages necessary for real-world applications while maintaining the proper electrochemical behaviour [14].

Hermann von Helmholtz initially offered and developed the idea of Electric Double Layer Capacitors (EDLCs) in the 19th century while researching how opposite charges behaved on colloidal particle surfaces. Helmholtz compared the electric double layer to a parallel-plate capacitor in his original model, in which the opposing charges, one in the electrolyte and one on the electrode surface, are organised in layers at the electrode/electrolyte interface and are only a few angstroms apart, or atomic-scale distances[22], [23]. Gouy and Chapman built on Helmholtz's work by proposing the idea of a dispersed layer to overcome this constraint. A more dynamic image, where the counterions are dispersed in a gradient away from the electrode surface instead of creating a fixed layer, results from their model's consideration of the thermal agitation of ions[23].

As the Gouy–Chapman model describes, the diffusive layer is established beyond the compact layer. A slow decrease in charge density with distance from the electrode surface is the result of thermal motion, or kinetic energy, affecting the distribution of counter-ions in this area. The resulting diffuse double layer is influenced by temperature, electrolyte content, and ion concentration, among other factors[24]. The capacitance of an EDLC is the combination of diffusion region capacitance and Stern layer capacitance. It is given by -

$$\frac{1}{C_{dl}} = \frac{1}{C_H} + \frac{1}{C_{diff}} \qquad \dots (v)$$

Electric Double Layer Capacitors (EDLC) are a type of electrostatic charge storage multimedia device, particularly in uses involving carbon-based electrode materials that may or may not fulfil electrochemical charge storage characteristics for charge storage, including activated carbons (AC), graphene, carbon nanotubes (CNT) and other carbon nanostructures. EDLCs distinct from Faradaic (redox) processes, it can store energy when charge then stored as charge separation occur at the electrode–electrolyte interface or build capacitance from electrodes relative to the charge storage in the double layer that develops on the electrode surface. Subsequently, carbon-based electrodes are believed to also exhibit high chemical stability, aiding their efficiency in different electrolytes affecting EDLC applications.

Carbon also has good electrical conductivity characteristics that allow for high power output while sustaining good electron transfer while being limited by internal resistance for effective high cycle electric quality needs. Electric Double Layer Capacitors (EDLC) use an electrostatic charge storage method, particularly when they use carbon-based electrode materials that are electrochemically inactive. These substances include activated carbons (AC), graphene, carbon nanotubes (CNT) and other carbon nanostructures.

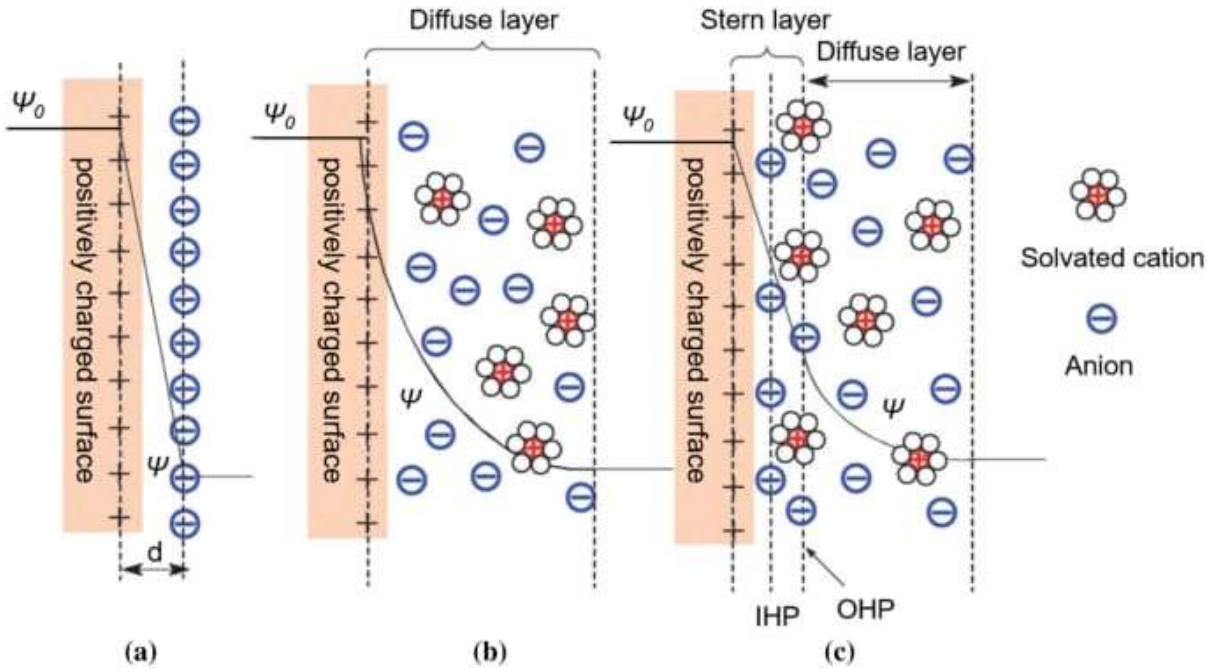

Fig. 1.6 Model for electrical double layer:(a) The Helmholtz model (b) The Gouy Chapman model (c) The Stern model[25]

1.7.2 Pseudo Capacitor (PC)

One kind of supercapacitor that uses conducting polymer electrodes, metal oxides, or metal chalcogenides as active materials is called a pseudocapacitor. Because of their capacity for quick and reversible redox (oxidation-reduction) processes, these materials have high electrochemical pseudocapacitance. Pseudocapacitors use Faradaic processes to store energy, in contrast to traditional electric double-layer capacitors (EDLCs), which use non-Faradaic electrostatic charge accumulation.

The Faradaic process involves a direct transfer of charge between the electrolyte and the electrode material, which is comparable to regular redox reactions. These redox processes are triggered at the electrode surface of a pseudocapacitor when an external potential is applied, which causes Faradaic current to flow through the cell. During the transfer of charge across the interface, this current represents the real motion of electrons and ions. Together with these redox reactions, an electrochemical double layer forms on the electrode material's surface. Compared to simply electrostatic supercapacitors, this results in an increased energy storage capability since the combined contributions of the electrostatic and Faradaic mechanisms increase the device's overall capacitance. The

bulk of the electric charge in pseudocapacitor (PC) devices is transferred to the electrode material or to the surface areas next to the solid electrode-electrolyte interface, where Faradaic reactions take place when the electrolyte contacts the active electrode material, resulting in voltage-dependent charge transfer processes. Therefore, the electrochemical behaviour of pseudocapacitors is intrinsically dependent on the applied voltage.

Pseudocapacitor-based ultracapacitors work by three main electrochemical processes: (1) electrolyte ion redox reactions, (2) electrolyte ion surface adsorption, and (3) doping and de-doping of conducting polymer (CP) components in the electrode matrix. Since more surface area usually results in more interaction sites, the first two mechanisms are surface-driven processes that are greatly impacted by the electrode materials' specific surface area. The third method, on the other hand—doping and de-doping conducting polymers—works in a bulk manner, so the material's surface area has less of an impact on its capacitance contribution. Rather, the bulk material's structural characteristics and inherent redox activity are more important. The electrode materials must have exceptional electronic conductivity to provide the best possible charge storage and delivery performance. Maintaining good power and energy performance in pseudocapacitor devices depends on this because it guarantees consistent current distribution and effective charge collection throughout the electrode during the charging and discharging cycles[26].

The specific capacitance and energy density of pseudocapacitors can also be substantially larger than those of electric double-layer capacitors (EDLCs). The main cause of this improved performance is the Faradaic charge storage process, which entails quick and reversible redox interactions between the electrolyte and electrode material. The solely electrostatic charge accumulation observed in EDLCs is not as efficient as these Faradaic processes, which allow both surface-level and bulk-level charge transfer[20].

1.7.3 Hybrids Supercapacitor (HSC)

Hybrid supercapacitors are a distinct type of energy storage device characterized by an asymmetric electrode configuration, whereby one electrode shows electrochemical activity through Faradaic processes, like in pseudocapacitors, while the other shows electrostatic behaviour like EDLC. The hybrid SC takes advantages of the

complementary benefits of EDLC and pseudocapacitors and thus able to avoid the limitations of both EDLC and pseudocapacitors when it used separately[27].

Hybrid supercapacitors exhibit a higher electrochemical performance such as increased energy density, increased specific capacitance and superior rate capability, by integrating EDLC and PC mechanisms into a single device. Demand for Hybrid supercapacitors are increasing due their customizable topology, increasing high energy density and improved electrochemical properties with extended cycle life. As such, hybrid supercapacitors are seen as a viable pathway for the next generation of supercapacitor technology transcending EDLCs in numerous applications[27].

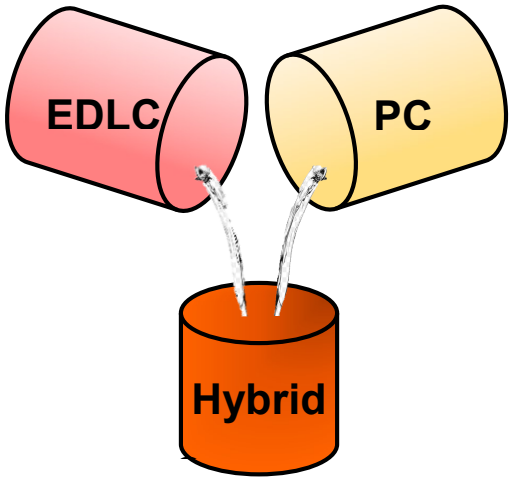

Fig. 1.7 Hybrids SC

Hybrid SC can be distinguished in three different types based on the variations in their electrode designs which are asymmetric, composite and battery-type.

1.7.3.1 Composite Hybrids SC

Carbon-based materials are increasingly being used with conducting polymers or metal oxides in supercapacitor composite electrodes. The combination makes it possible to have two types of processes for energy storage in a single electrode - Faradaic redox reactions for chemical energy storage and electrostatic interactions for physical energy storage[29]. The chemical process relies on a conducting polymers or metal oxides redox-active properties, the physical process mostly depends on the electric

double layer created by the high surface area and conductivity of the carbon materials[30].

1.7.3.2 Asymmetric Hybrids SC

Asymmetric hybrid supercapacitors connect an electric double-layer capacitor (EDLC) electrode and a pseudocapacitive electrode into a single unit that can effectively utilize both Faradaic and non-Faradaic charge storage mechanisms. Like EDLCs, this device generates an electric double layer at the interface between the electrode and the electrolyte and relies upon this non-Faradaic process for electrostatic charge storage. At the same time, the pseudocapacitive portion of this assembly permits Faradaic charge transfer via reversible, fast redox processes.

1.7.3.3 Battery Type Hybrids SC

Battery-type hybrid supercapacitors are a relatively unique example of a battery-type electrode combined with a supercapacitor (SC) electrode within one energy storage device. This new hybrid design attempts to combine the high energy density and longer energy release of a battery with the fast charging and discharging of a supercapacitor. These device types are intended to meet the increasing demand for energy storage devices that provide high energy and high-power performance.

The battery-type electrode provides higher energy density via bulk redox reactions, while the supercapacitor electrode provides fast charge storage and charge delivery via electrostatic or surface-confined Faradaic processes. Thus, the hybrid cell can demonstrate both battery-like and supercapacitor-like behaviours within a single device. Research into battery-type hybrid supercapacitors themselves has been limited, despite an enormous potential for battery-type hybrid supercapacitors.

1.8 Electrode material

Overall performance for supercapacitor (SC) applications can be maximized with careful selection and fabrication of the electrode material(s). The following are requirements for optimal electrode materials for SCs: corrosion resistance, chemical stability under a variety of conditions, high specific surface area (SSA) for maximum

charge storage, sufficient electrical conductivity for charge transport, and thermal stability. Importantly, there must be adequate surface contact area between the anode/cathode materials and the electrolyte for effective charge movement.

Optimal electrode materials should be economically viable, safe for large-scale use, and environmentally benign. In addition, many morphological and structural parameters are important for determining that electrode's specific capacitance. Deliberate control of morphology - pore size distribution, pore shape, pore diameter, etc. that have impacts how well the electrolyte ions can get to the active surface area. Enhanced ion transport and electrolyte diffusion through the porous structure can significantly improve the charge storage efficiency, making morphological design a key parameter to consider during the creation of high-performance supercapacitor electrodes[30].

Fig. 1.8 Different Electrode Material for Supercapacitor

1.8.1 Carbon based material

Carbon-based materials are often preferred as an electrode material when developing supercapacitors due to several beneficial properties. Carbon-based materials generally have a very high specific surface area; having a large enough surface area is critical to create a charge storage system. The low-production costs of carbon materials make them viable for large-scale processes. The abundance of carbon materials allows for a sustainable and readily available material upon process scale-up. The charge storage mechanism of carbon materials is another important aspect. This mechanism takes place as an electrochemical double layer is created at the interface between the electrode and electrolyte. Since charge is physically stored in this mechanism, faradaic (redox) processes are not necessary, meaning that the capacitance is mainly dependent on the surface area that the electrolyte ions can interact with.

Both structural and functional characteristics have a major impact on the electrochemical performance of carbon-based electrodes. These include the material's specific shape, surface area, pore size and distribution. The capacitance is increased by materials having a large specific surface area because they offer more active sites for charge accumulation. However, surface functionalization is also crucial to further improve the electrochemical behaviour because it can increase wettability and contribute in a pseudocapacitive way. Achieving high-performance supercapacitor electrodes requires optimizing these properties[30].

1.8.1.1 Graphene

Graphene, a unique allotrope of carbon, consists of one layer of carbon atoms organized in a two-dimensional honeycomb lattice with hexagonal symmetry. Unlike all other carbon allotropes, graphene is a polymeric carbon structure that has a sheet-like shape because it is only one atom thick. The incredible mechanical strength of this structure arises from the strong sp2 hybridized bonds that are formed between each carbon atom and the three adjacent carbon atoms. Graphene also results in a π-conjugated system with even greater electrical conductivity when the fourth valence electron of each carbon atom delocalizes throughout the sheet.

Graphene is especially attractive for applications such as supercapacitors because of its unique properties, including a very high specific surface area, exceptional chemical and thermal stability, and extraordinary electrical conductivity. Main advantages of graphene as electrode material is its independence from the pore distribution frequently required for optimal ion transport and charge storage. Even without a highly porous structure, the atomically thin structure of graphene, combined with high electron mobility allows for quick charge collection and transfer[14].

1.8.1.2 Carbon Nanotubes (CNT)

Carbon nanotubes (CNT) have unique pore structure, excellent electrical conductivity, thermal stability and outstanding mechanical strength that created a great deal of excitement as potential supercapacitor electrode materials .These one-dimensional nanostructures are comprised of rolled graphene sheets forming cylindrical tubes, with varying lengths and nanoscale diameters. The two forms of carbon nanotubes, namely single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), offer their own unique advantages for energy storage applications depending on the number of graphene layers.

Catalytic chemical vapor deposition (CVD) is the most widely used method for synthesizing CNTs. One of the benefits of CNTs over traditional carbon based electrode materials is their interconnected mesoporous network that promotes ion transport and enables charge to be uniformly distributed across the electrodes surface. This network structure ensures greater interaction with the electrolyte, improving rate performance and charge-discharge efficiency

CNT have excellent conductivity and structural properties, but their energy density, when considering their lower specific surface area, could hinder their overall energy storage capacity potential when compared to other materials such as activated carbon that have larger surface areas. Thus, CNT perform very well in power density and cycle stability, but their smaller surface area can be the main limitation in overall energy storage capacity. CNT are a promising material to be used in next-generation supercapacitor technologies, and if the electrochemical properties are optimized through

functionalization of the surface and optimization of structure and composites, the electrochemical performance could be improved[14].

1.8.1.3 Carbon Nanofibers (CNF)

Graphene sheets are single-atom thick layers of carbon atoms bonded in a hexagonal manner that can be rolled into seamless cylindrical structures with the longitudinal axis parallel to the graphene plane, therefore generating carbon nanotubes (CNT). When graphene sheets are stacked together with different orientations it will produce a carbon nanofiber (CNF), which can have several structural topologies. These sheets may be placed perpendicular to the fiber axis, coiled or angled (inclined) within the fiber. The heterogeneity of the internal structure strongly influences the physical and electrochemical properties of CNFs. Alternatively, CNFs can be produced without obtaining a crystalline graphene layer structure. In these examples, a polymer precursor like pitch, lignin or polyacrylonitrile (PAN) is used. Typically, electrospinning or solution spinning methods are completed, to produce small fibers from the polymer precursor. The fibers are then stabilized, before being carbonized at low temperatures, to yield amorphous carbon nanofibers[14].

1.8.1.4 Activated Carbon

Activated carbon (AC) is regarded as an ideal electrode material because of its extremely high surface area, high electrical conductivity and low cost. Activated carbon can be synthesized from carbonaceous source materials such as industrial waste, biomass or agricultural by-product materials. The two approaches that define the synthesis of activated carbon are chemical activation and physical activation. In the chemical activation process, the precursor material is mixed with activating chemicals, like potassium hydroxide or phosphoric acid and heated to high temperature, which helps develop pores. The physical activation process leads to porous structure formation by oxidizing agent gasification of raw material after the precursor material is carbonized at high temperature[32].

1.8.2 Metal Oxides

The most widely researched transition metal oxides for pseudocapacitor electrode purposes are vanadium pentoxide (V_2O_5), nickel oxide (NiO), ruthenium oxide (RuO_2),

manganese dioxide (MnO_2) and cobalt oxide (CoO_4). These metal oxides have increased capacitance due to their ability to undergo multiple reversible redox processes at specific potentials. These redox processes significantly affect their pseudocapacitive behaviour.

Specifically, ruthenium oxide (RuO_2) has gained much attention for its unique combination of features. RuO_2 has excellent thermal and chemical stability, outstanding electrochemical redox properties, high catalytic activity and electrical conductivity comparable to metals. Further increasing its potential is RuO_2's ability to act in both crystalline and amorphous states. Due to these unmatched features, RuO_2 has significant importance in the wide variety of applications in ferroelectric thin films, electronic components, development of integrated circuits and the fabrication of both thin-film and thick-film resistors[33]. RuO_2 is a prominent efficient metal oxide that remains under investigation as electrode materials for various applications. Its prolonged operational life, broad electrochemical potential window, highly reversible oxidation-reduction processes and extremely high specific capacitance are primarily responsible for this. RuO_2 has metallic-type conductivity, which contributes to improving its utility as an electrode material for use in supercapacitors. The electrochemical electrodeposition method has been a popular method used for making RuO_2 for supercapacitor (SC) applications. As an example of the impressive performance of these electrodes using such a method, a specific capacitance of 498 $F \cdot g^{-1}$ at a scan rate of 5 $mV \cdot s^{-1}$ and excellent cycling stability over tens of thousands of charge-discharges[33].

1.8.3 Metal Chalcogenides (MC)

The anisotropic aspect of metal chalcogenides (MC) has been the focus of considerable attention for the last 20 years due to their many uses in industry and science. The layered crystalline structure found in these compounds is composed of metal and chalcogen elements and consequently endows them with unique directional properties. These stable layered binary crystalline phases of MC typically contain transition metals located in groups IV to VII B and chalcogen elements in group VI A such as sulfur (S), selenium (Se), and tellurium (Te). The individual layers of MC are held together by only weak van der Waals forces, which allow them to adopt a two-

dimensional structure that has mechanical exfoliation potential and tunable electrical properties.

Their band gap, which is a crucial parameter to define them as semiconductor, is related to the electrical properties of these materials. Transition metal chalcogenides have a variety of band gaps. The band gap in MC is influenced by the number of atomic layers in the structure, the specific combination of metal and chalcogen elements, the presence of dopant atoms, functionalization in the absence and many more variables. Nevertheless, for the most part, transition metal chalcogenides have many similarities with graphene. In the past few years, the study of transition metal chalcogenides (MCs) has grown tremendously due to their improved safety about regular batteries and their long-term stability and longer working life cycle.

Many beneficial properties provide (i) a longer cycle life, which provides good long-term durability; (ii) a high density of reactive surface sites, which provides more overall electrochemical activity; (iii) structural flexibility, which may allow better integration with a range of architecture for devices; (iv) improved electrical conductivity, which decreases internal resistance and ohmic losses; (v) shorter electron transport paths, which allows faster charge-discharge; and (vi) the occurrence of quantum-size effects which improve their overall electrochemical behaviour at the nanoscale[35].

Metal sulfides can be distinguished from other kinds of MC materials primarily by their impressive electrochemical properties. Many features of metal sulfides, such as better electronic conductivity, superior electrochemical reactivity, mechanical and thermal properties, lead to a proposed superiority over the many other candidate materials. From these properties, metal sulfides display characteristics that are excellent candidates for next-generation energy storage devices. Extensive research has already established that factors such as the size, crystalline phase, structural morphology, chemical composition and design of the electrode used in the electroactive material all play a significant role in the performance of electrochemical energy storage devices [36]. In this respect, metal selenides have recently come forth as a promising new class of electrode materials for batteries. Due to certain qualities like their spectacular mechanical and thermal stability, extensive redox potential and tremendous electrical conductivity, metal selenides are gaining popularity as supercapacitor electrodes. Given

their unique properties, they are outstanding candidates for emerging energy storage technologies[37].

1.8.4 Metal Sulphide (MS)

Metal sulfides (MS) have drawn considerable interest as promising electrode materials for energy storage devices due to their unique structural and electrochemical characteristics. MS, a distinctive family of compounds, consisting of metal cations and sulfur anions typically exhibit high electrical conductivity, narrow band gap and multiple oxidation states that allow very fast redox reactions. The engagement of sulfur networks contributes additional pathways for electron transport and provide faradaic charge storage behaviour. Their abundantly available and low-cost nature also provides MS with a comparative advantage on scalability and sustainability for next generation energy storage devices such as supercapacitors and batteries[38].

The mixed metal sulfides (MMS) include many redox-active centers that can potentially offer stronger electrochemical performance relative to conventional electrode substances such as metal oxides (MO) and carbon-based compounds. The reason why MMS would be more effective is likely due to the sulfur content, which enhances flexibility and encourages effective electron transfer. MO and carbon material frequently present limitations such as low volumetric capacitance, especially for low density electrodes, agglomeration issues and challenges to fabricate [39]. The charge transport behaviour of MS is primarily attributed to their interlayer gap and arrangement; as with the multitude of physicochemical characteristics of metallic sulfides, if an adequate interlayer gap does not afford enough space for ion diffusion, then their overall electrochemical properties and commercial viability will be diminished. Most current research initiatives are still unable to address this critical facet [40].

Their use in high-performance supercapacitor systems, however, merits more research. During charge-discharge cycles, MSs experience faradaic reactions because of their tiny band gap and active redox characteristics. This improves charge storage, but it also restricts energy density, decreases the operating voltage window, and compromises cycling stability. Incorporating bigger anions with higher anionic polarizability can help to alleviate these disadvantages by boosting overall electrochemical kinetics and ionic diffusivity. The integration of theoretical simulations and mathematical modeling is

expected to be crucial in directing the logical design, optimization, and scalable synthesis of MS-based materials in addition to experimental methods. The creation of high-performance, reasonably priced electrodes with specialized structural and electrical characteristics may be made possible by such initiatives. Notwithstanding advancements, methods aimed at adjusting the physical and chemical characteristics of MSs are still desperately needed in order to enable their useful integration into clean, green, and renewable energy storage technologies [37].

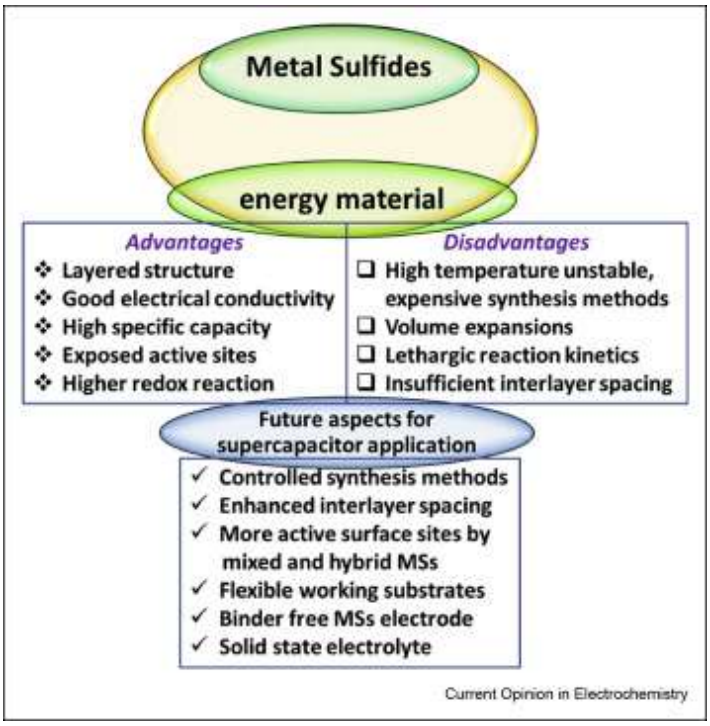

Fig. 1.9 Schematic presentation of challenges and future aspects for metal sulfides as energy material[38]

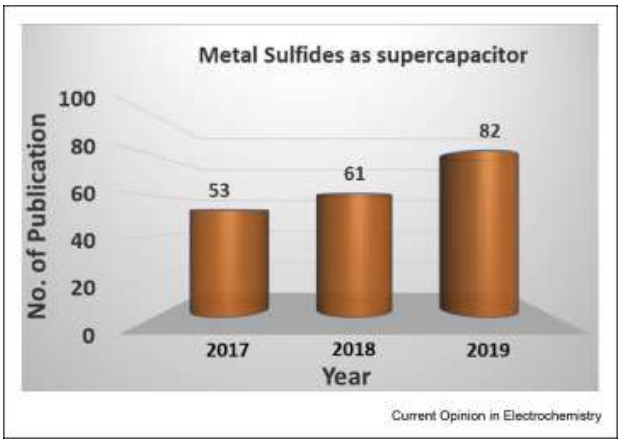

Fig. 1.10 Number of publications for metal sulfides as supercapacitor[38]

1.9 Electrolyte

The electrolyte is essential to the operation of supercapacitors because it permits ionic conductivity, which makes it easier for charge carriers to travel between the electrodes. It usually comprises of a mixture of an electrolyte salt and an appropriate solvent. A number of variables affect the electrolyte's efficacy and efficiency, including as the ions' size and kind, their interactions with electrode surfaces, solid-to-solid contacts, and operating pressure levels. Furthermore, the total performance of the supercapacitor is greatly impacted by the electrolyte's electrochemical stability window[39]. It makes it possible to choose the electrolyte that works best with a certain electrode material, increasing the device's capacity to store energy and overall effectiveness.

1.10 Aim and Objective of this present work-

- ✓ To synthesize the Cobalt Sulphide from Tridax Procumbens leaf extract.
- ✓ Synthesis of Cobalt Sulphide based electrode.
- ✓ To study the structural and morphological characterization of Cobalt Sulphide.
- ✓ The electrochemical study of Cobalt Sulphide based material electrode by cyclic voltammetry, Galvanostatic charge-discharge, and Electrochemical impedance spectroscopy to find the specific capacitance, resistance.

CHAPTER 2: LITERATURE SURVEY

Many works have gone into finding effective electrode materials that can deliver high energy and high power simultaneously since they are crucial in determining the performance of SC. Cobalt sulfide (CoS)-based materials have gained significant attention as potential electrode materials for supercapacitors due to their diverse oxidation states, fast redox kinetics, high theoretical specific capacitance, and excellent electrochemical activity [40]. Various stoichiometric forms such as CoS, CoS_2, Co_9S_8, and Co_3S_4 exhibit different physicochemical properties and energy storage behaviors. The performance of these materials is largely influenced by their morphology, crystallinity, particle size, and surface area, which can be optimized through controlled synthesis methods such as hydrothermal, solvothermal, MOF-derived conversion, chemical bath deposition (CBD), and cathodic exfoliation techniques[41].

For instance, CoS nanoparticles synthesized via hydrothermal treatment at 200 °C demonstrated a high specific capacitance of 1583 F/g due to improved surface area and electroactive sites[42]. Additionally, CoS nanosheets derived from metal-organic frameworks (MOFs) and directly grown on nickel foam exhibited a specific capacity of 1359 C/g and retained 89.4% of their initial performance after 4000 charge-discharge cycles[43]. To further improve energy storage performance, structural engineering approaches have been explored. One such approach involves forming core/shell structures, such as ultrathin CoS nanosheets coated on $NiCo_2S_4$ nanotube arrays. These composites have shown areal capacitances of 4.74 F/cm² at 5 mA/cm² and excellent long-term stability[44]. The incorporation of conductive materials like carbon nanotubes (CNTs) and vertically aligned graphene enhances the conductivity and rate capability of CoS electrodes. For example, Co_9S_8 embedded in a CNT-carbon nanofiber matrix achieved a specific capacitance of 1656 F/g with 92.6% retention over 10,000 cycles[45].

Cobalt sulfide-based electrodes have also demonstrated great potential in practical applications such as asymmetric supercapacitors and flexible, high-temperature energy storage devices. Asymmetric supercapacitor configurations employing CoS on nickel foam with activated carbon have reached energy densities up to 57.4 Wh/kg[43]. Hollow NiAs-type CoS structures have shown high areal capacitance (260 mF/cm²) and excellent thermal stability, making them suitable for wearable electronics.Furthermore,

nanoporous carbon/CoS composites have achieved capacitance values of 677 F g^{-1} and energy densities of 23.5 Wh/kg with strong long-cycle retention[46]. As the need for environmentally friendly and sustainable solutions grows, green synthesis has become a competitive alternative to conventional chemical methods for creating cobalt sulfide (CoS) nanostructures. Biological agents like plant extracts, microbial cultures, and natural polysaccharides are used as reducing and stabilizing agents in green synthesis methods, as opposed to conventional techniques that frequently use high temperatures, hazardous chemicals, and energy-intensive procedures. Environmental safety, cost-effectiveness, scalability, and biocompatibility are just a few benefits that these methods provide[47].

In recent studies, various plant extracts have been successfully employed to synthesize cobalt sulfide nanoparticles. For instance, Leaf extract of Tridax procumbens served as a reducing and capping agent in the environmentally friendly CoS nanoparticles synthesis using a mild temperature regime (60–100 °C), producing spherical nanoparticles that were well-crystallized [52]. The supercapacitor electrodes demonstrated a specific capacitance of 1135 F g^{-1} at 1 A g^{-1} and demonstrated good cyclic stability, making them a good candidate for supercapacitor application [53]. Other plant-based methods have used Azadirachta CoS synthesis. They are phytochemicals with active components, flavonoids, alkaloids and polyphenols which can reduce cobalt salts to sulfide forms yet still act as capping agents to limit agglomeration.

Furthermore, green synthesis can be combined with composite strategies to improve performance even further. CoS nanomaterials synthesized in this work with Ocimum sanctum extract have also been combined with activated carbon or graphene and have showed improvements in conductivity, rate capability and energy density[48].

Recent advancements in cobalt sulfide (CoS)-based electrode materials expanded with new synthesis approaches and structural engineering techniques, which substantially improved their supercapacitor performance. For example, synthesized cobalt sulfide nanosheets based on metal–organic frameworks (MOF) directly onto nickel foam. This resulted in high-performance, binder-free electrodes due to the direct growth on the conductive substrate, which provided structural integrity and efficient electron transport during charge–discharge cycles[43]. Similarly, Pu et al. (2014) reported the direct growth of $NiCo_2S_4$ nanotube arrays on nickel foam to create an electrode without a binder which

showed high specific capacitance and excellent cycling stability. Binders were removed due to their likelihood of reducing electrical conductivity and providing pathways for ions to better move through the electrode adsorbent resulting in overall performance being vastly improved in the supercapacitor system[49].

S. Aloqayli et al produced Cobalt sulfide (Co_9S_8) from sulfurized phase-pure nanostructured cobalt oxide (Co_3O_4) and had notable increased energy storage properties. The Co_9S_8 electrode had high areal capacitance of 7358 mF cm^{-2} , which was much higher than Co_3O_4. They studied electrochemical performance and the Co_9S_8 electrode had excellent flexibility and stability with no loss of function when bent. A supercapacitor device fabricated using Co_9S_8 showed remarkable cycling stability up to 5000 cycles and a ~100% increase in capacitance when the temperature was raised from 10 to 70 °C, highlighting its potential as a high-performance, flexible, and binder-free electrode material for energy storage applications[50].

Hu-Lin Li et al synthesized cobalt sulphide by electrochemical technique, charge discharge behavior was discovered with high specific capacitance of 475 F g^{-1} at current density of 5 mA/cm2[51].

Rajendran Ramachandran et al synthesized CoS and graphene nanocomposites using cobalt nitrate, thioacetamide, and graphene as starting ingredients, with poly(vinylpyrrolidone) as a surfactant. XRD analysis confirms the amorphous nature of the nanocomposites. The nanocomposites demonstrated outstanding capacitive performance when CV was performed at various scan rates over a potential range of 0 to -0.8 V. A maximum specific capacitance of 2423.3 F g^{-1} was achieved at a scan rate of 5mV/s[52].

A novel CQDs/CoS_2 nanocomposite was synthesized using a solvent-free ball milling approach followed by solvothermal treatment[53]. The carbon quantum dots (CQDs) were derived from glycerol via a green, catalyst-free microwave-assisted method, yielding ~16%. The resulting nanocomposite exhibited a unique edge-brick-like morphology, high specific surface area (427.2 m^2 g^{-1}), and enhanced mesoporosity and electronic conductivity. These structural advantages contributed to an impressive specific capacitance of 808 F g^{-1} at 1 A g^{-1}, along with excellent rate capability (83.9% retention at 20 A g^{-1}) and outstanding cycling stability (98.75% over 10,000 cycles). The study

highlights the potential of CQD/CoS_2 as a promising electrode material for high-performance energy storage devices.

A simple method was stated for synthesizing functionalized spongy graphene/cobalt sulfide (FG-CoS) nanocomposites with a porous 3D crinkly-sheet structure, incorporating CoS nanoparticles between reduced spongy graphene oxide layers. The FG-CoS composites confirmed a high specific capacitance of 1072 F g^{-1} at 1 mV s^{-1} and excellent cycling stability with 117% retention after 1000 cycles. The composite attained an energy density of 35.2 Wh kg^{-1} and a power density of 250 W kg^{-1}. These enhanced electrochemical performances were attributed to the synergistic interaction between graphene and CoS, making FG-CoS a potential candidate for high-performance supercapacitor electrodes [60].

Nanostructured Co_XS_X, $Ni_{17}S_{18}$ and $(CoNi)_3S_4$ materials were synthesized via a one-step hydrothermal method to investigate their use as energy storage materials. The study highlighted the influence of morphology—fibrous, flake-like and sheet-like—on electrochemical performance. Among them, the amorphous CoxSx showed the highest specific capacitance of 57 F g^{-1} with 76% retention after 1000 cycles, compared to 31 F g^{-1} for crystalline $(CoNi)_3S_4$. These findings demonstrate the importance of structural form and composition in enhancing supercapacitor performance [61].

A green and simple solution-based synthesis route was reported for the fabrication of flower-like $Co_{1-x}S$ nanostructures using L-cysteine as both a chelating agent and sulfur source. The formation of hierarchical nanosheet-based architectures was attributed to the presence of diethanolamine as a solvent. The $Co_{1-x}S$ electrode exhibited a specific capacitance of 674 F g^{-1} at 3 A g^{-1} and retained 548 F g^{-1} after 1000 cycles at 5 A g^{-1}, indicating excellent rate capability and cycling stability. These results highlight the potential of $Co_{1-x}S$ nanostructures as efficient supercapacitor electrode materials [62].

$NiCo_2S_4$ and carbon– $NiCo_2S_4$ heterostructure nanosheet arrays were synthesized on nickel foam via a hydrothermal method followed by CVD processing. These materials were formed through anion exchange reactions from NiCox(OH)y and carbon–$NiCo_2O_4$ precursors in Na_2S solution. The carbon– $NiCo_2S_4$ composite exhibited superior electrochemical properties, with a high specific capacitance of 1893.2 F g^{-1} and areal capacitance of 8.33 F cm^{-2} at a mass loading of 4.4 mg cm^{-2}. Furthermore, an

asymmetric supercapacitor assembled using carbon– $NiCo_2S_4$ as the positive and activated carbon as the negative electrode achieved a high energy density of 68.82 Wh kg^{-1} at a power density of 47.83 W kg^{-1}, indicating strong potential for practical energy storage applications. Hence the Nickel and Cobalt Sulphide can be considered as a feasible candidate for the manufacture of supercapacitor electrode [63].

Apart from the type of the electrode material, the electrochemical performance of supercapacitors is directly influenced by their morphological, dimensional, surface chemical, porosity, and electrolyte type. Green synthesis, particularly using plant extracts, offers a sustainable, cost-effective, eco-friendly alternative, simple and biocompatible when compared to physical and chemical synthesis methods.

CHAPTER 3: EXPERIMENTAL WORK

The plant Tridax procumbens is utilized in this work to produce cobalt sulphide.

Fig. 3.1 Tridax Procumbens Plant

3.1 Tridax procumbens

The medicinal plant Tridax Procumbens, which belongs to the Asteraceae family, is often referred to as coat button, kansari (Hindi), or ghamara. Mostly utilized in Indian traditional medicine, this herb is also used by several groups. The species is highly promising and produces secondary metabolites like alkaloids, steroids, carotenoid, flavonoid (catechins, centaurein, and bergenins), fatty acids, phytosterols, tannins, and minerals. These compounds have been scientifically screened for a number of medicinal uses, including antibacterial, anti-inflammatory, antimicrobial, vasorelaxant, antitileishmanial, antianemic, immunomodulatory, hepatoprotective, and mosquitocidal properties. (TP)

Tridax procumbens, a widely available medicinal plant, contains bioactive compounds such as flavonoids, alkaloids, tannins, and phenolics, which can act as reducing and stabilizing agents in nanoparticle synthesis. This plant grows abundantly in many areas, especially in hot and moist climates.

3.2 Advantages of Tridax Procumbens

1. Rapid growth rate
2. Widely available
3. Antioxidant
4. Antimicrobial
5. Wound healing potential
6. Versatile application
7. Cost effective

3.3 Method of Cobalt Sulphide synthesis

There are different method to synthesis Cobalt Sulphide. Despite the excellent electrochemical properties of cobalt-based materials, conventional synthesis methods often involve toxic chemicals, high-temperature treatments, and energy-intensive processes, leading to environmental concerns. To address these issues, Green Synthesis has emerged as a sustainable and eco-friendly alternative for nanoparticle fabrication. Plant-mediated synthesis offers a simpler and more convenient green synthesis approach compared to microbe- or fungi-mediated methods.

3.4 Green Synthesis of Cobalt Sulphide

Green synthesis, particularly using plant extracts, offers a sustainable, cost-effective, eco-friendly alternative, simple and biocompatible when compared to physical and chemical synthesis methods [54]. Plants are known to contain biomolecules such as enzymes, proteins, amino acids, vitamins, polysaccharides, and organic acids such as citrates that are potentially able to reduce metal ions. This method has been used mostly for metallic and oxides nanomaterial[55]. Plants extracts contain natural reducing, stabilizing, and capping agents such as flavonoids, alkaloids, tannins, and phenolic compounds, which facilitate nanoparticle formation without the need for harsh chemicals. ***Tridax procumbens***, a widely available medicinal plant, contains bioactive compounds such as flavonoids, alkaloids, tannins, and phenolics, which can act as reducing and stabilizing agents in nanoparticle synthesis. This plant grows abundantly in many areas, especially in hot and moist climates. One of the advantages of the plant meditated synthesis of nanomaterials amongst other green methods, is the high yield[56].

3.5 Material used-

- Tridax Procumbens plant
- Cobalt Nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$)
- Thioacetamide (CH_3CSNH_2)
- Acetone (C_3H_6O) and ethanol (C_2H_5O)
- Nickel Foam
- Deionized water (DI water)
- Polyvinylidene fluoride (PVDF), Acetylene black and N-methyl-2 pyrrolidone (NMP)

3.6 Preparation of Tridax Procumbens Plant Extract

Healthy and fresh leaves of Tridax procumbens were collected. The leaves of Tridax procumbens were washed three times with regular water and then rinsed with deionized water. 300ml of deionized water was added to the beaker containing a magnetic needle. The leaves were then added to the beaker placed on a heating and stirring (at 60°C for 24 hours). This extract was filtered through Whatman filter paper and then consecutively used in the green synthesis.

3.7 Synthesis of Cobalt Sulphide NPs

0.75 g of Thioacetamide was added to 25 mL of filtered extract in one beaker and 2.13 g of cobalt nitrate hexahydrate to another beaker of 25 mL filtered extract. Both beakers were stirred until the solutes dissolved. The solution of Thioacetamide was added dropwise to the cobalt nitrate solution causing it to turn black colour. The mixture was then stirred for 6 hours at 70°C. It centrifuged and calcined at 300°C yields the NPs.

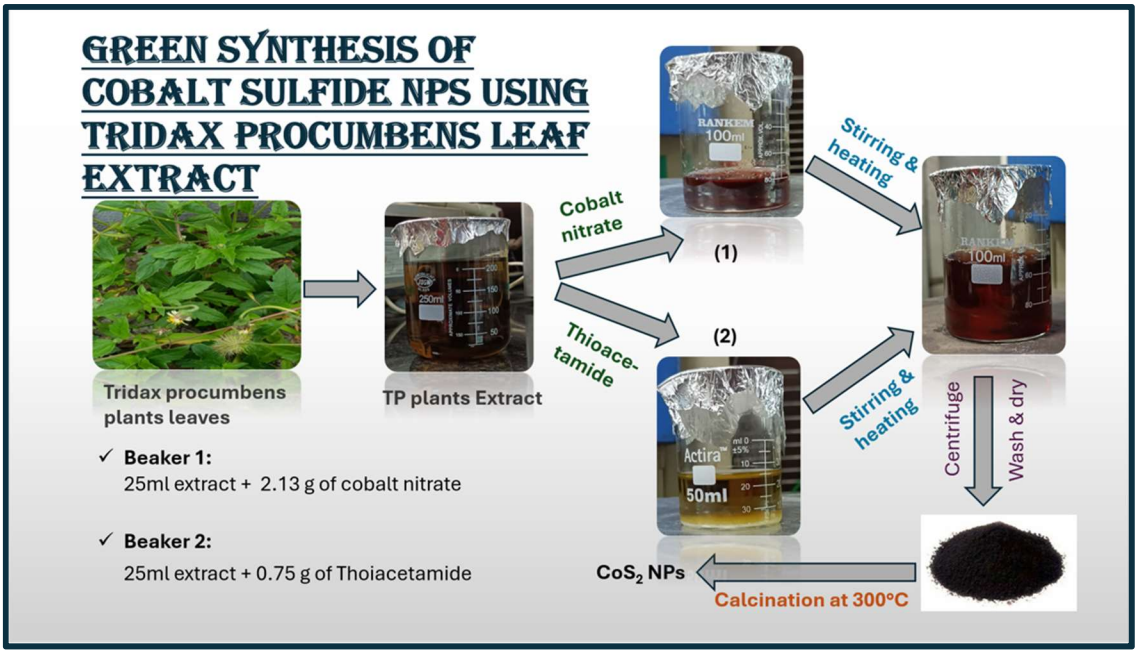

Fig. 3.2 Green synthesis of Cobalt Sulfide NPs using Tridax procumbens leaf extract

3.8 Fabrication of Cobalt Sulphide Material Electrode

Nickel foam was utilized as the current collector, to prepare the working electrode. The nickel foam surface was first treated by sonicating it in a 2 M HCl solution and then washing it in each of deionized water and acetone for 15 minutes. The surface oxide layer was effectively removed by this process, and the nickel foam was vacuum-dried at 80°C for 6 hours to prevent additional oxidation. Then Polyvinylidene fluoride (PVDF), acetylene black and CoS_2 were then combined in an NMP (N-methyl 2-Pyrolidone) solution at an 8:1:1 mass ratio to create a slurry for the working electrode. After that the slurry is drop cast upon Ni foam (4 cm×1 cm) that has been prepared. Then electrode was dried in an oven for 6 hours at 80°C. Using the gravimetric weight difference method, the mass loading on the working electrode was determined to be 7mg.

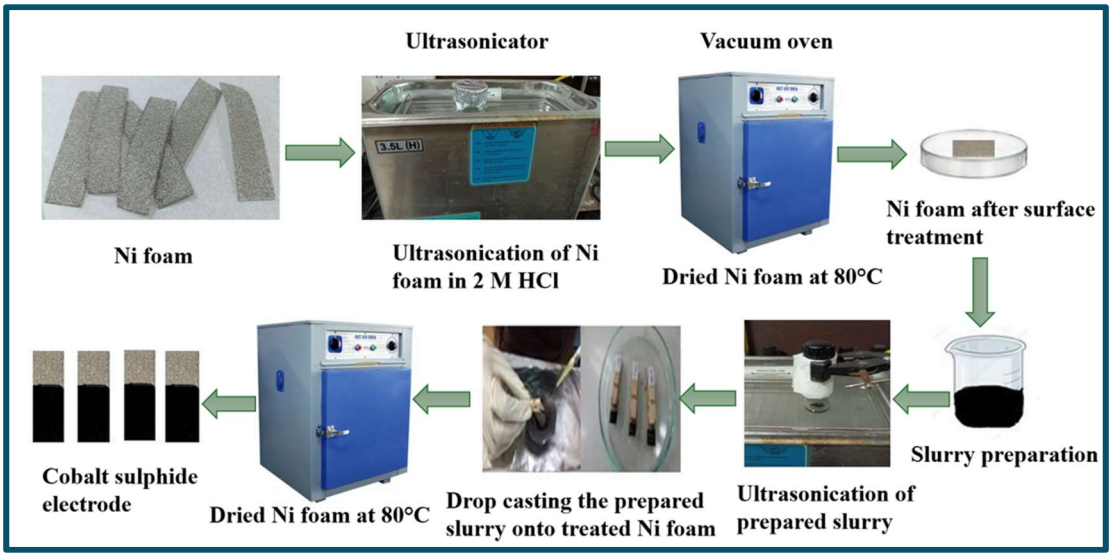
Ultrasonicator
Vacuum oven
Ni foam
Ultrasonication of Ni foam in 2 M HCl
Dried Ni foam at 80°C
Ni foam after surface treatment
Slurry preparation
Ultrasonication of prepared slurry
Drop casting the prepared slurry onto treated Ni foam
Dried Ni foam at 80°C
Cobalt sulphide electrode

Fig. 3.3 Schematic diagram of fabrication of Cobalt Sulphide based electrode

3.9 Characterization Techniques

Various characterization techniques were investigated to study the physical and chemical properties of the material. An understanding of the chemistry and physics of materials requires a study of characteristics such as structure, surface morphology, electrical, thermal, mechanical, optical, etc. We have used XRD examine the structural characteristics of the produced Cobalt Sulphide NPs in this work. Electrochemical characterization techniques like CV, GCD, and EIS are conducted to determine specific capacitance of the electrode.

3.9.1 Xray- Diffraction

XRD was performed by equipment model XRD- D8 Quest system bruker diffractogram. X-ray powder diffraction (XRD) is a fast analytical technique that is primarily utilized to distinguish phases and unit cell dimension inside a crystalline material. The material being examined is homogenized, finely ground, and its average bulk composition is determined. A crystalline sample and constructive interference from monochromatic X-rays are the source of X-ray scattering (XRD). These monochromatic X-rays are produced by a cathode ray tube and are directed towards the crystalline sample after being filtered to produce monochromatic radiation and collimating it toward the sample to focus. If Bragg's condition is satisfied, the incident ray interacts with the sample, which results in constructive interference (as well as a diffracted wavelength).

$$n\lambda=2dsin\theta \qquad ...(vi)$$

Where, n is the integer, λ is the wavelength of the x-ray used, d is the interplanar distance, and θ is the diffraction angle.

The diffraction angle, lattice spacing of crystal and wavelength of electromagnetic radiation are interconnected by this Bragg's law. Then we can detect, evaluate, and count these diffracted X-rays. As the arrangement of the material is random, that is powdered, all directions of potential lattice diffraction can be determine by sample scanning through a range of 2θ angles. Identification of the compound is possible by conversion of the diffraction peaks to d-spacings values because each compound has a particular set of d-spacings. To do this, d-spacings are compared to common reference patterns[57].

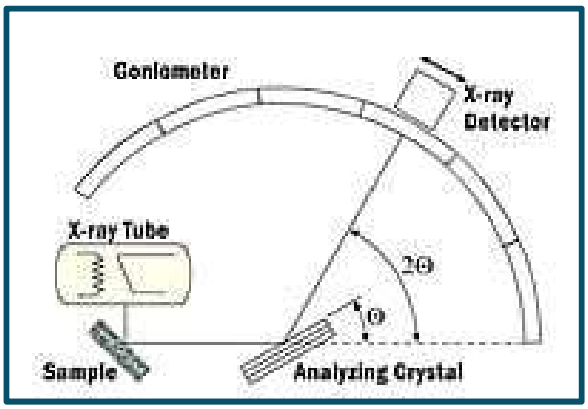

Fig. 3.4 Schematic diagram of x-ray diffractometer[57].

3.9.2 Scanning Electron Microscopy (SEM)

To investigate the morphology of the sample Scanning electron microscope (JEOL Model JSM-7600F) is utilized. A scanning electron microscope, or SEM, produces sample images by scanning its surface with a concentrated electron beam. An electron beam is thermionically emitted in a standard SEM setup by an electron cannon equipped with a tungsten filament cathode. Since tungsten has the highest melting point of any metal and emits electrons when heated, it is the substance preferred for cannons of thermionic electrons. Lanthanum hexaboride (LaB_6) cathodes are one kind of alternate electron emitter. One or two condenser lenses are used to focus the electron beam, which normally has a voltage between 0.2 and 40 keV, into a spot with a width of 0.4 to 5

nm. The electrons interactions with the sample's atoms result in a variety of signals that provide details on the sample's composition and surface topography. The detected signal is combined with other information to create an image, where the electron beam is scans in a raster scan pattern[58].

SEM can produce incredibly precise images at high magnifications of up to 300,000x and even 1000000 (in certain contemporary versions) for a broad variety of materials. A high-energy electron beam with an electron voltage between 100 and 30,000 volts will be used to do the analysis.

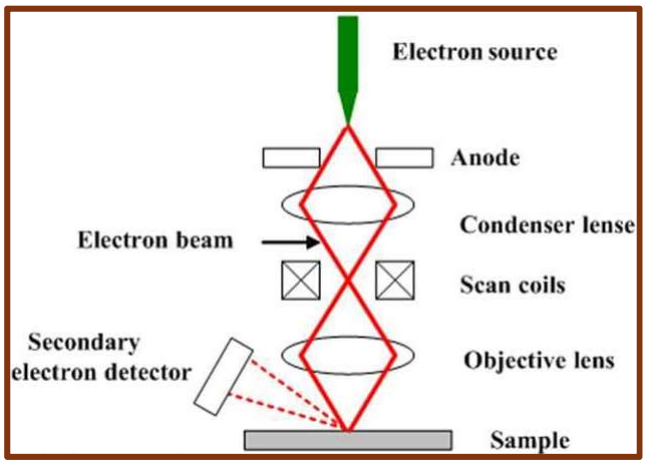

Fig. 3.5 Instrumentation and working of Scanning Electron Microscopy

3.9.3 Energy -Dispersive X-ray Spectroscopy (EDS)

To get a localized chemical analysis, EDS uses the X-ray spectrum that is produced when a solid sample is subjected to an intense electron beam. While not all equipment can detect 'light' elements ($Z < 10$), theory suggests that every element from atomic number 4 (Be) to 92 (U) can be identified. Consideration must also be given that qualitative analysis is straightforward for X-ray spectra in that the path to achieving this subjective analysis is simply to identify the lines in the spectra. Whereas, the process of a quantitative analysis is to measure the line intensities for each element exemplified in the sample, then the equivalent elements in the calibration Standards of known composition, to obtain the concentrations of the identified elements.

Element distribution images are created in a "mapping" mode by scanning the beam in a two-dimensional raster pattern like a television and displaying the intensity of a selected X-ray line. Depending on the mode selected, differences in surface

topography, or variations in mean atomic number, can also be viewed in the images produced.

3.10 Potentiostat for Electrochemical performance

To evaluate the electrochemical performance of resultant sample cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) measurements were conducted in a three-electrode system in 3M KOH as a electrolyte. An electrical device called a potentiostat is made to maintain the electrochemical stability of a sensor while transforming its output into an analog signal. This device, as shown in Figure 3.6, consists of three electrodes immersed in an electrolyte a reference electrode that keeps the electrolyte at a known potential; a counter electrode; and the working electrode, where the desired oxidation or reduction reaction takes place and biomolecular probes can be attached. A platinum (Pt) wire is usually used as the counter electrode while Hg/HgO is often used as the reference electrode. A reference electrode is only used as a reference to establish and regulate the working electrode voltage; it never conducts current. The counter electrode, on the other hand, receives all of the current needed to balance the current observed at the working electrode.

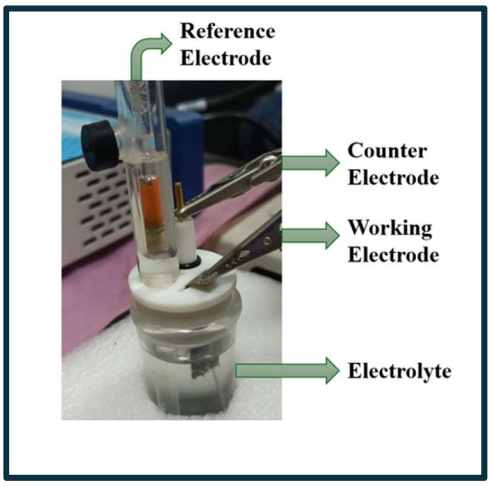

Fig. 3.6 Schematic diagram of electrochemical setup

3.11 Electrochemical measurements

3.11.1 Cyclic voltammetry

Cyclic voltammetry is one of the most used methods to examine the electrochemical behaviour of electrodes and helps us determine capacitance. In general, it is an electric current test in which the potential of the working electrode increases linearly with time. The working electrode is immersed in the electrolyte (3M KOH) and has the potential to be utilized in electrochemical system was provided between working and reference electrode, during current measurement between the working electrode and the counter electrode[59], [60]. How rapidly modifications are made depends on the test's scanning speed. The current is stronger as the speed rises because the diffusion process's extent diminishes.

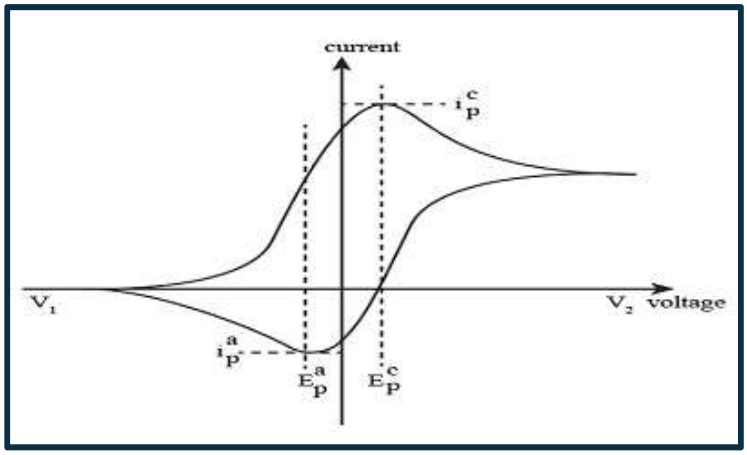

Fig. 3.7 Cyclic voltammogram

Typical CV curves associated with varying single-electrode reactions are shown in the figure. Here V_1 and V_2 are limiting potentials, V_{PC} and V_{PA} are the cathode and anode peak voltages, respectively, and I_{PC} and I_{PA} are the cathode and anode peak currents. The reduced capacity is used during forward transmission, increasing to a certain value (from time t_1 to time t_2). When the device's reduction potential is reached, the cathodic current drops and the concentration of leftover analyte is depleted. Change refers to the voltage at point t_2, since the measurement is done in reverse here. Reducing the analytes at the reverse scan rate re-oxidizes from time t_1 to t_2 that creates a negative current called the anodic current. The choice of potential window (e.g., initial voltage and final voltage) is very important since the operating potential of the supercapacitor depends on the redox potential and dissociation potential nature of the electrolyte solution.

As discussed in the previous section, supercapacitors commonly use the EDLC mechanism and pseudocapacitive mechanism. An ideal EDLC capacitor gives a rectangle CV curve, while a pseudocapacitor shows a redox peak in the CV curve. The formula used for calculation of specific capacitance (Cs) is given in Eq.(vii)

$$C_s = \frac{A}{mK(V_2 - V_1)} \qquad \ldots (vii)$$

Where, C_s is the specific capacitance, K is scan rate, m is mass of electrode materials, $(V_2 - V_1)$ is potential window and A is area under the curve.

3.11.2 Galvanostatic charge-discharge (GCD)

Galvanostatic charge-discharge (GCD) is sometimes referred to as "chronopotentiometry" since it differs greatly from CV, which records the potential in response to time at constant current. To enable the maximum number of charge-discharge cycles without resulting in noticeable specific capacitance losses, the current density and discharge time parameters should be chosen. The amount of current determines how many charge-discharge cycles may be obtained by galvanostatic studies. From the GCD the specific capacitance was calculated using Eq.(viii)

$$C_S = \frac{I \times \Delta t}{\Delta V \times m} \qquad \ldots (viii)$$

Where, C_S is the specific capacitance, I is the current, m is mass of electrode materials, Δt is the discharge time and ΔV is the potential window.

At first, the supercapacitor is discharged to a preset voltage, which is frequently near 0V. The galvanostat is used to apply a steady current to the supercapacitor. The intended rate of charge is usually used to determine the current. Throughout the charging process, the supercapacitor's voltage is continuously checked. When the voltage hits a preset level, often the device's maximum safe voltage, charging is terminated. After the charging process, the supercapacitor is allowed to rest briefly to stabilize. In the opposite direction (discharge), a steady current is applied. By changing the direction of the current, this can be accomplished using the same galvanostat. Throughout the discharging process, the voltage across the supercapacitor is continuously measured. When the voltage hits a

preset minimum value, which is frequently near the starting voltage, the discharge is stopped[61].

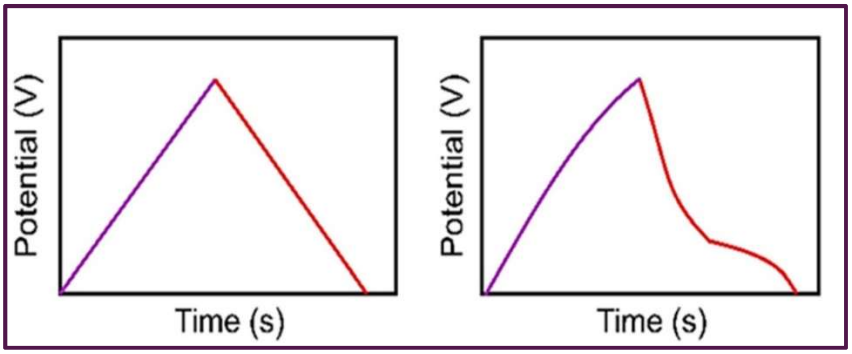

Fig. 3.8 Charging and discharging mechanism (a) EDLC and (b) Pseudocapacitor

3.11.3 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy can effectively explore the electrochemical behaviour of energy storage systems in significant ways. EIS measurements can measure system quality without affecting it. EIS allows us to determine the electrochemical process's equilibrium constant. EIS is often conducted with open-circuit voltage conditions, frequencies between 0.1 Hz and 100 kHz, and very modest AC potential amplitudes (5 to 10 mV). The simple AC resistance of the battery is known as impedance (Z), and its formula is $Z = Z' + jZ''$; the real and imaginary components of the impedance are denoted by Z' and Z''. Resistance is represented by the real component, and capacitive and inductive behavior is represented by the imaginary part[62].

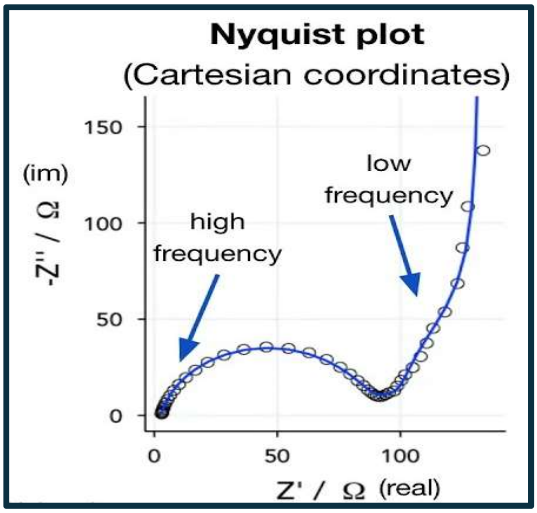

Fig. 3.9 Electrochemical impedance spectroscopy

The Nyquist plot is the most often used method for analyzing EIS data. It is a plot of real impedance (Z') against imaginary impedance (Z"). Three sections make up the EIS diagram's main view: the high frequency, mid frequency, and low frequency sections. Together, they make up the internal resistance (RS) system. The electrolyte resistance is represented by the high-frequency semicircle area, and the electrode resistance is represented by the semicircle's commencement at high frequencies. The diffusion mechanism is represented by a line bent at a 45° angle at midfrequency; the optimal capacitive ion diffusion is represented by an A-line bent at 90°. Interfacial charge transfer resistance (RCT) results from charge transfer and ion diffusion into the pores of the electrode material. Therefore, balanced circuits provide a clear understanding of the different processes that occur in energy storage [63], [64].

CHAPTER 4: RESULT AND DISCUSSION

4.1 Structural Characterization

4.1.1 X-ray Diffraction Analysis-

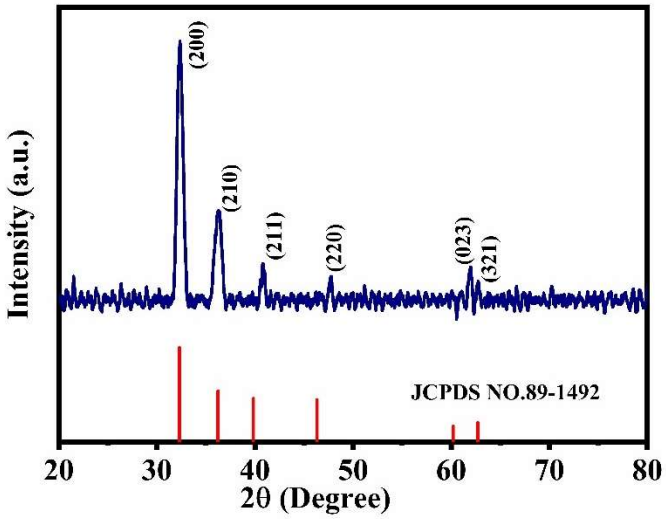

Fig. 4.1 XRD Spectra of the CoS_2 Sample

The confirmation of sample crystalline structures was achieved through analysis of the XRD patterns. The XRD pattern of the synthesized CoS_2 NPs have been demonstrated in Fig.4.1 XRD pattern indicates the phase purity of synthesized CoS_2 NPs. The 2θ peaks have been appeared at 32.35°,36.24°, 40.82°, 47.68°, 61.90° and 62.75° and their corresponding (hkl) values have been assigned 200, 210, 211, 220, 023 and 321 respectively. The XRD pattern of synthesized CoS_2 NPs compared with JCPDS database. The XRD pattern of synthesized CoS_2 NPs matches with JCPDS No.89-1492 which crystallizes in primitive cubic structure with a Pa-3 space group and lattice parameters of 5.538 A°.

4.2 Morphological characterization

4.2.1 Scanning Electron Microscopy (SEM) Analysis-

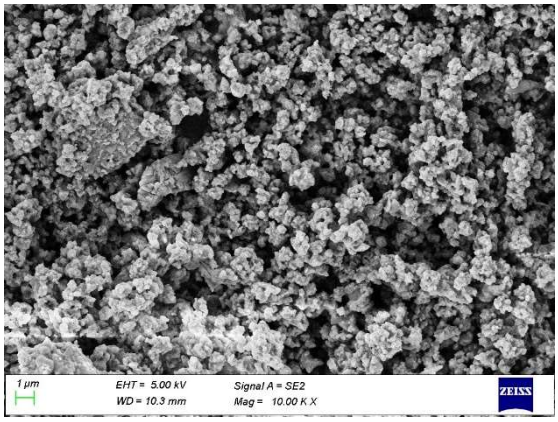

Fig.4.2 SEM image of CoS_2 electrode

The surface morphology of CoS_2 electrode is explored by SEM. Figure 4.2 shows SEM image recorded on the surface of the sample. As shown, the massive structure of precursor can prevent agglomeration so that nanostructure was obtained that consists of fine particles.

4.2.2 Energy Dispersive Spectroscopy (EDS) Analysis-

EDS analysis elemental composition is depicted in Fig.4.3, The EDS data shows the elements content in the CoS_2 sample namely Cobalt (Co) and Sulphur(S). Sulphur dominate the sample with atomic percentages is 54.40 % and Cobalt having 45.60 % respectively.

Table (2) - Atomic weight % of elements in CoS_2 NPs

Element	Atomic weight %
Co	54.40
S	45.60

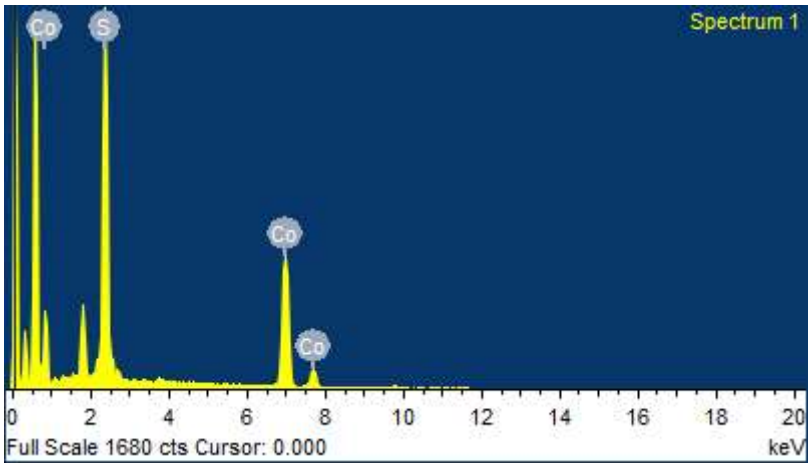

Fig. 4.3 EDS Spectrum of CoS_2 Nanoparticles

4.3 Electrochemical characterization

The electrochemical performance of the synthesized materials was studied using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS).

4.3.1 Cyclic Voltammetry-

The electrochemical study has been done using cyclic voltammetry techniques. The CV curves have been recorded at different scan rates at 5 mV s^{-1} , 10 mV s^{-1} ,20 mV s^{-1} , 30 mV s^{-1},40 mV s^{-1} ,50 mV s^{-1} ,75 mV s^{-1} ,100 mV s^{-1} and 150 mV s^{-1} which are given in Fig. 4.4, We have determined the specific capacitance of synthesized CoS_2 NPs.

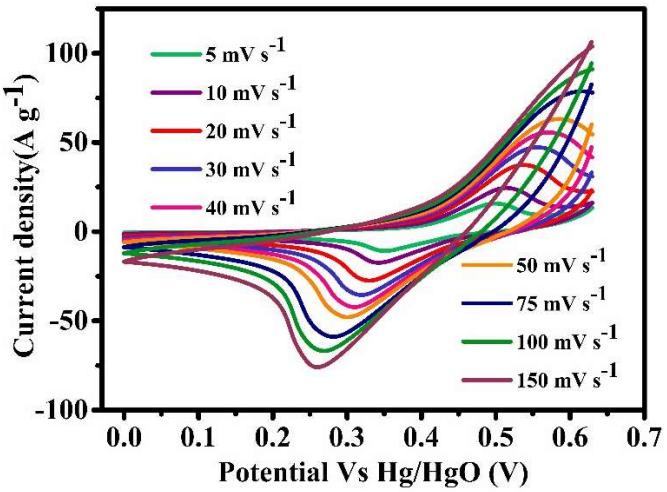

Fig. 4.4 CV curves at variable scan rates

The obtained values of specific capacitance for synthesized CoS_2 NPs are 1612 F g^{-1} at 5 mV s^{-1}, 1243 F g^{-1} at 10 mV s^{-1} , 982 F g^{-1} at 20 mV s^{-1} , 861 F g^{-1} at 30 mV s^{-1} , 786 F g^{-1} at 40 mV s^{-1} ,731 F g-1 at 50 mV s^{-1} , 626 F g-1 at 75 mV s^{-1} , 547 F g-1 at 100 mV s^{-1} and 428 F g-1 at 150 mVs^{-1} respectively. These values are reported in Table (3) respectively. It shows the values of specific capacitance decreases with increasing scan rates from 5 mV s^{-1} to 150 mV s^{-1}. It means at very low scan rates the synthesized CoS_2 NPs get charges efficiently. Specific capacitances were calculated for different scan rates as shown in table

The formula used for calculation of specific capacitance (Cs) is given in Eq.(ix)

$$C_S = \frac{A}{mK(V_2 - V_1)} \qquad \ldots (ix)$$

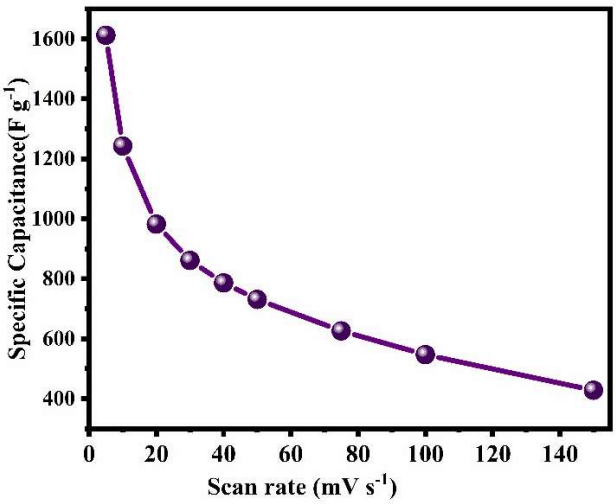

Fig. 4.5 Specific Capacitance Vs Scanning Rates

Table (3) - Specific Capacitance of CoS_2 electrode at different scan rates

Sr. no.	Scan Rate ($mV\ s^{-1}$)	Specific Area	Specific Capacitance ($F\ g^{-1}$)
1	5	5.0792245	1612
2	10	7.8306848	1243
3	20	12.369247	982
4	30	16.276695	861
5	40	19.797170	786
6	50	23.0144839	731
7	75	29.5636414	626
8	100	34.4900511	547
9	150	40.4808785	428

4.3.2 Galvanostatic Charge-Discharge Analysis-

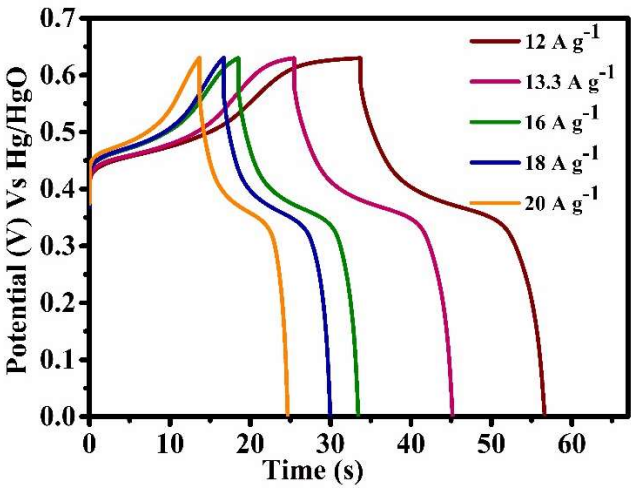

Fig. 4.6 GCD curves at different current density

The GCD profile of the synthesized CoS_2 NPs for different current densities is shown in Fig. 4.6, From the GCD the specific capacitance was calculated using Eq.(x)

$$C_S = \frac{I \times \Delta t}{\Delta V \times m} \qquad \ldots (x)$$

Where Cs is the specific capacitance, I is the current, m is mass of electrode materials, Δt is the discharge time and ΔV is the potential window. The obtained values of specific capacitance for synthesized CoS_2 NPs are 604.47 F g^{-1} at 12 A g^{-1} , 431.96 F g^{-1} at 13.34 A g^{-1}, 393.90 F g^{-1} at 16 A g^{-1}, 377.14 F g^{-1} at 18 A g^{-1} and 372.06 F g^{-1} at 20 A g^{-1} respectively. The higher specific capacitance seen at 12 A g^{-1} & lower at 20 A g^{-1} therefore we can say that specific capacitance decreases with increasing current density.

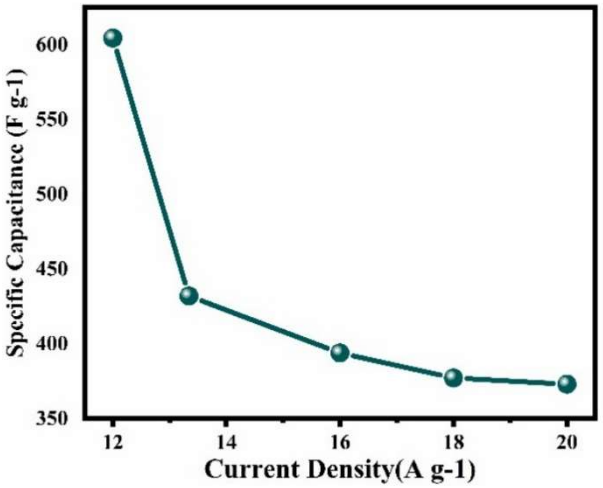

Fig. 4.7 Specific Capacitance Vs Current Density

Table (4) - Specific Capacitance of CoS_2 electrodes at different Current Density

Sr. no.	Current Density (A g^{-1})	Discharge Time (s)	Specific Capacitance (F g^{-1})
1	12	31.84	604.47
2	13.3	20.40	431.96
3	16	15.51	393.90
4	18	13.20	377.14
5	20	11.72	372.06

4.3.3 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy is used to observe an electrode material's frequency response with open-circuit potential, the EIS measurements were carried out in the frequency range of 100mHz–100MHz. The results as shown in Fig.4.8 demonstrated the Nyquist plot along with the fitted equivalent circuit.

When studying the Nyquist plot, a straight line is found at low frequency zone and a semicircle is obtained at high frequency zone. The point where the graph contacts the x-axis gives the value of solution resistance (Rs). The solution resistance involves the resistance resulting from the aqueous KOH electrolyte, the intrinsic resistance of electrode material, and the interface resistance caused by the contact between the active electrode material and the current collector (Rct). The straight line corresponds to the Warburg diffusion resistance (W).

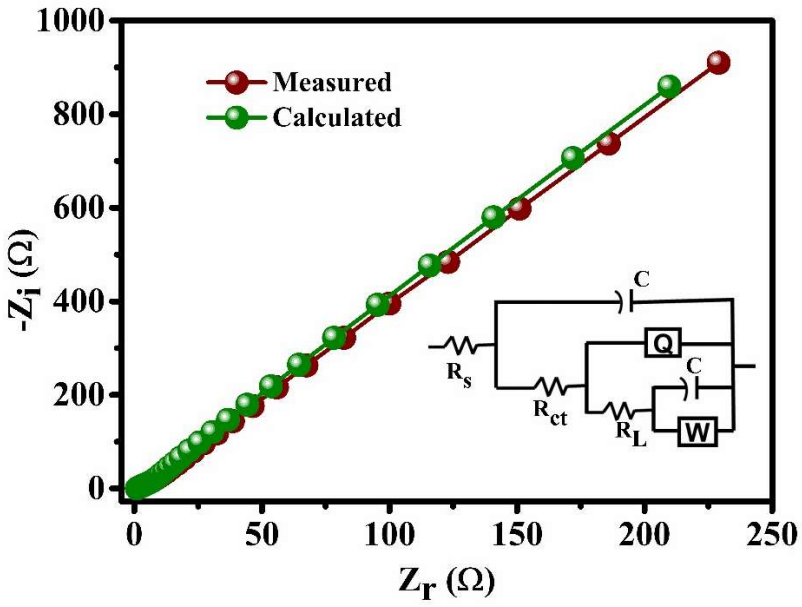

Fig. 4.8 Nyquist plot of CoS_2- material based electrode.

Smaller values of these indicate higher electrochemical responsiveness and offer good conducting pathways for rapid electron passage. From the Nyquist plot, the value of Rs and Rct is found to be 1.035Ω and 0.01Ω respectively, which implies the excellent electrical conductivity with constant phase element(Q) is 0.001471.

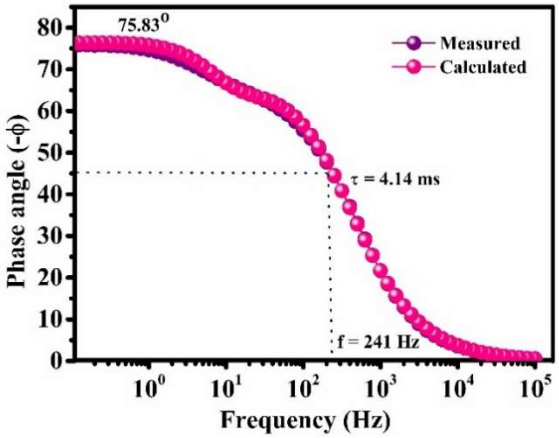

Fig. 4.9 Bode Phase Plot of CoS_2- material based electrode

The frequency response of electrode material studied using Bode plot. A phase angle of 45◦ indicates diffusion-controlled behaviour of the electrode material, whereas a phase angle of 90◦ generally indicates pure capacitive properties. In the case of a phase angle of approximately 75.83◦, as observed in Fig. 4.9, it clearly indicates the pseudocapacitive nature of the electrode. This supports the conclusions drawn from the GCD and CV measurements, which show that localized redox reactions close to the electrode surface are primarily responsible for the capacitance. The relaxation time constant (τ_0) was calculated using Eq.(xi)

$$\tau_0 = \frac{1}{f_0} \qquad \ldots (xi)$$

Where, f_0 is the frequency corresponding to the 45◦ phase angle. The value of τ_0, which is equal to 4.14 ms, indicates that rapid release of stored energy by the electrode.

4.3.4 Cyclic Stability

A stability test demonstrates the extended performance of the developed electrode material. In Fig. 4.10 shows the cyclic stability of capacitance retention decreases gradually upto 3000 cycles. The cycling stability behaviour of the CoS_2 sample indicated that it retained 81.18 % of its original capacitance upto 1000 cycles, 71.3 % of its original capacitance upto 2000 cycles and 58.46 % of its original capacitance upto 3000 cycles.

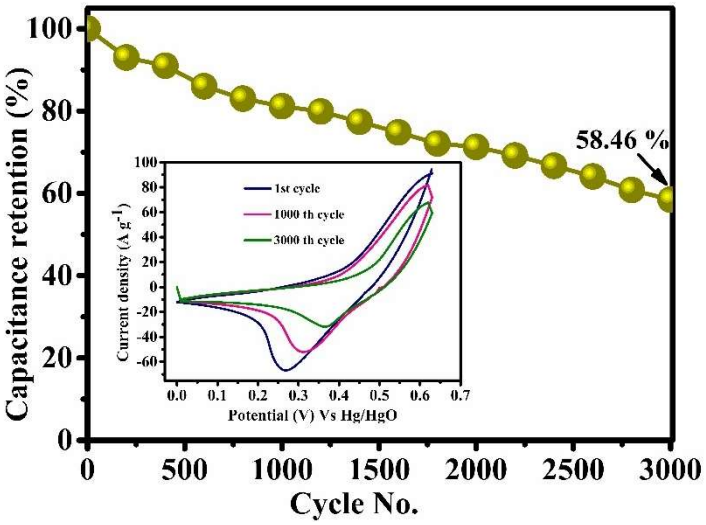

Fig. 4.10 Cycling stability of CoS_2 based electrode

CHAPTER 5: CONCLUSION

The synthesis of CoS_2 NPs using an aqueous extract from the Tridax procumbens plant was accomplished in a simple, cost-effective, and ecofriendly greener approach. The XRD results showed the primitive cubic structure of CoS_2. With increased annealing temperature and better crystallinity, the size of the crystallites was observed to rise. The electrochemical energy storage capability studies showed that the CoS_2 NPs annealed at 300 °C gave the best specific supercapacitance of 1612 F g^{-1} at 5 mV s^{-1}. The resulting nanoparticles can be used as an electrochemical energy storage electrode material. The specific capacitance of CoS_2 based electrode found to be 604.47 F g^{-1} at current density of 12 A g^{-1} in 3M KOH electrolyte. These outstanding electrochemical properties of CoS_2 made it a promising electrode material for supercapacitor application.

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15 सितम्बर 1860 - 12 अप्रैल 1962